

A novel integrated process for the functionalization of methane and ethane: bromine as mediator

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Available online 8 October 2004

Abstract

We describe a novel, integrated multi-step process for the partial oxidation of alkanes to alcohols, ethers or olefins using O₂ as oxidant. The sequential transformations are (1) alkane bromination to alkyl bromide(s) and HBr, (2) reaction of this mixture with solid metal oxide (MO) to neutralize the HBr and to generate oxygenated products or olefins plus solid metal bromide, and (3) oxidation of the spent solid with O₂ to regenerate the metal oxide and Br₂ for reuse.

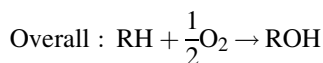
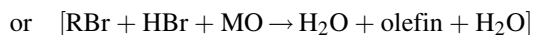
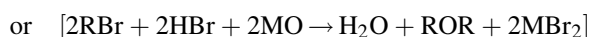
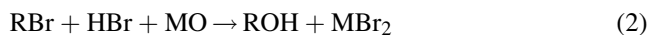
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Keywords: Bromine-mediated; Partial oxidation; Alkane; Metal oxide

1. Introduction

Efficient transformation of alkane feedstocks to more valuable oxygenated or unsaturated compounds continues to represent an important intellectual challenge with strong economic rationales [1]. Here we describe a novel, integrated multi-step process for the partial oxidation of alkanes to alcohols, ethers or olefins using O₂ as oxidant, illustrated in Scheme 1. The sequential transformations carried out in a flow reactor are alkane bromination to alkyl bromide(s) and HBr (Eq. (1)), reaction of this mixture with solid metal oxide (MO) to neutralize the HBr and generate oxygenated products (alcohols or ethers) or olefins plus solid metal bromide, (Eq. (2)), and lastly oxidation of the spent solid with O₂ to regenerate the metal oxide and Br₂ for reuse (Eq. (3)). Thus, the ultimate oxidant is dioxygen. The process may be applied as a platform technology for

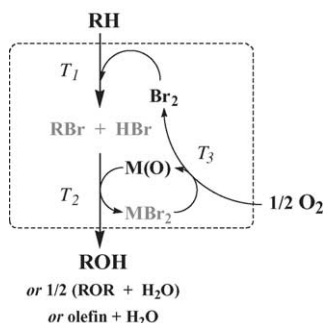
virtually any alkane partial oxidation process.



The key to the successful partial alkane oxidation reported here is the use of a solid transition metal oxide (or MO mixture) on a stable support to react with the alkyl bromide and effect bromide/oxide metathesis under mild conditions. While others have considered related approaches [2–5] – for example, Olah et al. [3] described electrophilic catalysis of methane halogenation followed by hydrolysis to give CH₃OH and (CH₃)₂O – the integration of all the steps into

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Scheme 1.

a single scheme using a sequential zone flow reactor (SZFR) is unique. Furthermore, the MO composition strongly influences product distribution and thus provides product control, especially with feedstocks other than methane. For example, with ethane certain MO compositions and reaction conditions give mostly alcohols or ethers, while others give predominantly ethylene or acetaldehyde. Finally, alkyl bromide coupling to higher alkanes/olefins/aromatics together with HBr neutralization is possible through the use of composite metal oxide/zeolite materials (see below). Hence, virtually any reaction that may be considered a partial oxidation may be performed by this platform technique.

2. Results and discussion

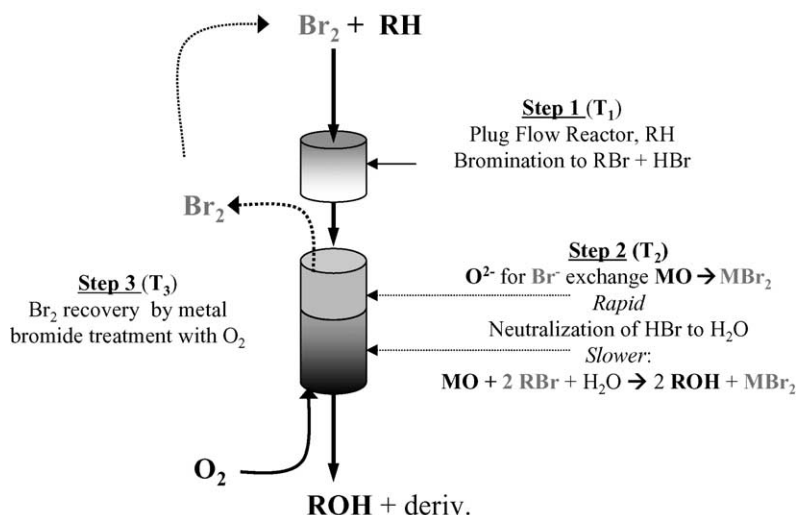
2.1. Bromine mediated partial oxidation to oxygenates and olefins

The SZFR consisted of two serial reactors, Scheme 2. In the first, a stream of Br_2 and excess alkane (1–3 bar) reacted at a temperature sufficient to convert 100% of the bromine. The resulting alkyl bromide(s), HBr and excess alkane were directed into the second reactor containing supported metal

oxide at 150–450 °C. The exiting products were identified and analyzed by ^1H NMR and GC (with MS, TCD or FID detection) techniques. Longer runs demonstrated that most of the (non-support) oxide equivalents can be utilized. After the metathesis capacity is largely consumed, O_2 was passed into the second reactor at 250–525 °C to regenerate the MO and Br_2 , the temperature depending on the specific metal oxide used. Redox active first row transition metal bromides/oxides tend to regenerate at a lower temperature than alkaline earths, for example. This procedure also released CO_2 from carbon deposited during the metathesis reaction. Repetitive runs (>50) cycles showed no significant loss of activity for the MO solids. Material balances were established for bromine by hypobromite ($300 \text{ M}^{-1} \text{ cm}^{-1}$ at 330 nm) analysis of the caustic regeneration trap and for carbon by quantitative GC and carbonate ($\text{Sr}(\text{CO}_3)_2$ gravimetric) analysis of the caustic regeneration trap.

Examples of effective solid reactants used for oxide/bromide metathesis are 50/50 CuO/ZrO_2 (MO-1) and 43/7/50 $\text{Co}_3\text{O}_4/\text{Sm}_2\text{O}_3/\text{ZrO}_2$ (MO-2) [6]. Products from these two differed considerably. MO-1 gave predominantly alcohols and more deep oxidation to CO_2 , while MO-2 gives largely ethers. For example, a 10:1 methane: Br_2 feed to a reactor containing MO-1 (3.6 g) led to 8.1% conversion of methane with comparable amounts of CH_3OH (37%), CO_2 (35%) and unconverted CH_3Br (29%) in the product stream. A similar run with MO-2 gave CH_3OH (20%), $(\text{CH}_3)_2\text{O}$ (20%), CO_2 (5%), and unconverted CH_3Br (40%) and CH_2Br_2 (15%). Reaction of pure CH_3Br with MO-1 or MO-2 generates some CO_2 due to reduction of metal center oxidants ($\text{Cu}(\text{II})$ or $\text{Co}(\text{III})$, respectively). Larger CO_2 yields in the integrated system can be attributed to reactions of polybrominated methanes, and thus can be addressed by improving bromination selectivity, either by introducing electrophilic catalysis or by otherwise optimizing reaction conditions.

SZFR experiments with ethane: Br_2 streams give less CO_2 and a richer product array. EtOH and Et_2O are the principal



Scheme 2.

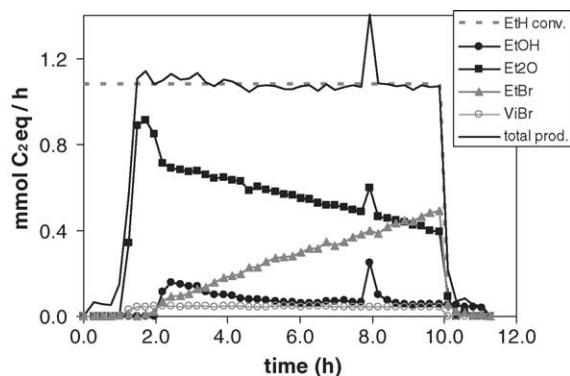


Fig. 1. Temporal output for ethane partial oxidation in a SFZR run. Ethane flow = 5.0 sccm; Br₂ flow = 0.50 sccm; pressure = 15 psig; bromination temperature = 350 °C; metathesis temperature = 200 °C. A solid reactant with the empirical formula Co₃Zr₃O₁₀ is used. * marks small amount of condensed water/ether/ethanol product entering the dilution/evaporation/dead volume chamber upstream from the gc.

products; other products include ethylene, acetaldehyde, vinyl bromide, ethyl acetate, acetone and butadiene, as well as unreacted EtBr. The relative yields are sensitive to MO composition and other reaction conditions. For example, MO-1 favors EtOH, MO-2 favors Et₂O, and raising temperature enhances ethylene formation.

Fig. 1 illustrates a SZFR run with a 10:1 ethane:Br₂ input (14.7 psig total pressure, reactor 1 at 350 °C) and MO-2 (8 g) in the second reactor (200 °C) which gave 9% ethane conversion. The temporal profiles for ether (49% of total products), ethanol (7%), unconverted EtBr (18%) and “other products” (CO₂ (2%), ethylene (6%), vinyl bromide (4%), butadiene (2%) and acetaldehyde (0.5%)) are shown. In the regeneration, adsorbed carbon (14% of C₂ equivalents consumed) was also demonstrated. At higher temperatures the product distribution resulting from the same feed shifts to a greater proportion of elimination products, Fig. 2. At

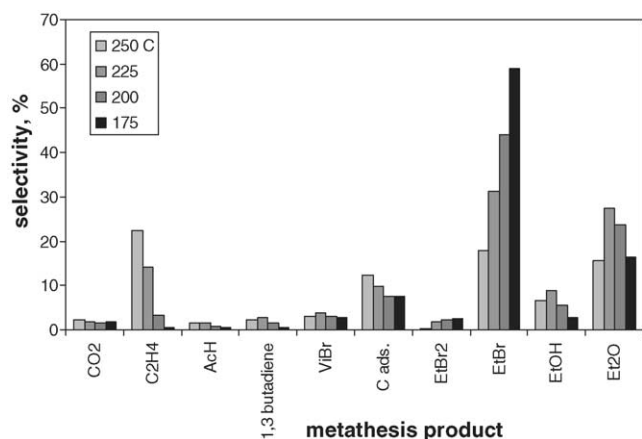


Fig. 2. Temperature dependence of bromine mediated ethane partial oxidation product distribution from a sequential zone flow reactor with a feed of 10:1 bromine:ethane. Ethane bromination goes to exhaustion of bromine in the first section of the reactor (350 °C, 10 s), while the temperature of the second section consisting of the solid oxide metathesis reagent (5 g, Co₃Zr₃O₁₀, the same materials as used in Fig. 1 is varied as shown.

350 °C, only ethylene (90%), vinyl bromide (5%) and CO₂ (5%) are observed products.

As stated above, the metal oxide morphology and composition also affect the metathesis product distribution under a given set of conditions, so the ability to test a wider range of systematically varied metal oxide formulations is of great value. We have built such an apparatus that allows us to semi-quantitatively evaluate the product distributions under identical temperature and pressure for 24 different solids at once, using synchronized stream selectors and GC injection valves. Under conditions of incomplete conversion of EtBr intermediate, we can compare the reactivity and product distribution of various solids, as shown in Fig. 3. Some of the solids tested favor ethanol production, suggesting highly reactive/nucleophilic hydroxyl functionality, some favor ether, which suggests a combination of nucleophilic and acidic character of the solids, while some give other side products such as acetone, acetaldehyde, and ethyl acetate, all of which represent further oxidation of EtX, either as a result of over-bromination and metathesis, or redox activity of the solid reactant.

2.2. Methane coupling

Utilization of methane as a chemical feedstock begins in practice with its conversion to methanol by partial oxidation to syngas followed by recondensation to Fischer-Tropsch products or CH₃OH. Conversion of CH₃OH to olefins was made possible by discoveries in the early seventies by Mobil scientists [7–10], and later generalized by other workers to CH₃X condensation (X = halide, SH, NH₂, OCH₃) [11–20]. The proposed mechanism [21,22] is an initial dehydrative coupling to form the actual catalyst, a relatively ill-defined adsorbed cyclic hydrocarbocation (carbon pool). The technology has been widely developed for multiple product

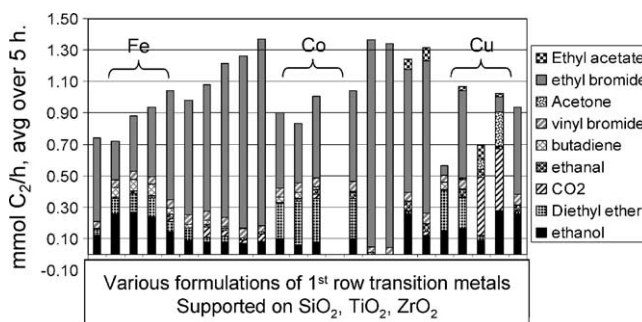
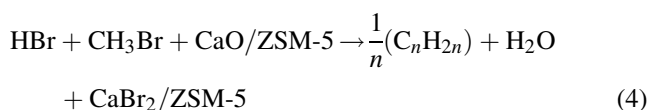


Fig. 3. High throughput testing of metathesis product distribution for bromine mediated ethane oxidation over supported transition metal oxide formulations. Note the broad range of products depending on the oxide. Ethane flow through each tube = 5 sccm. Br₂ flow = 0.5 sccm. Ethane bromination in each tube occurs in the upstream section over glass beads at 350 °C. Various cataloreactants (5 g, ~20 mmol active oxide) contained in downstream section of each tube at 225 °C. Products detected over the course of 5 h by GC with automated stream selection, with approximately 1 chromatogram per tube per hour.

outputs, and may be considered an alternative to the steam cracking method of olefin production from low and middle petroleum distillates. For CH_3Cl , formed from CH_4 oxychlorination, the product in most cases is an aromatic-rich liquid together with HCl and water [13–14] with some variation depending on the promoters used [15–20]. While this chloromethane chemistry has been well characterized and the kinetics are favorable, the process has not been commercialized. Although economical techniques exist for large scale centralized methane conversion to higher value chemicals, there is currently no cost effective way of recovering stranded methane, and further work to advance methane conversion technology could solve this long-standing inefficiency.

During the course of development of active and regenerable metathesis materials, oxides of calcium were investigated because of their lack of facile redox activity (leading to deep oxidation), stoichiometric HBr neutralization capacity, and the nearly thermoneutral regeneration of CaBr_2 with O_2 to give CaO and Br_2 ($\Delta G^\circ = 14.9$ kcal/mol). We observed that while activated HZSM-5 (Si:Al = 80) rapidly lost catalytic CH_3Br coupling activity over the course of 10 min, calcium oxide zeolite composites (see below) quantitatively neutralized HBr and effected the presumably superacidic condensation of methyl bromide to higher olefins (Eq. (4)).



We have shown previously that a stream of methane and bromine may be transformed into higher hydrocarbons, water and sequestered recoverable bromine by sequential bromination at 400–525 °C followed by flowing the bromo-carbon/ HBr product over CaO/ZSM-5 composite [23]. The selectivity for non-aromatic output improves if the feed composition becomes richer in CH_3Br . Fig. 4 shows the time dependent product output from a feed of CH_3Br (0.6 sccm) and methane carrier (5 sccm) over a bed of

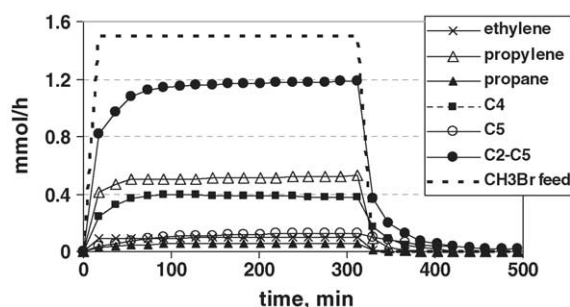
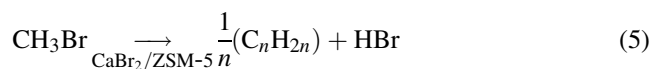


Fig. 4. CH_3Br condensation to olefins over a 10 mm $\times$ 100 mm plug of CaO/ZSM-5 (5 g) at 400 °C. Feed, $\text{CH}_4:\text{CH}_3\text{Br}$ (5.0:0.6 sccm); space time = 20 s, WHSV = 0.025 h^{-1} . Selectivity to $\text{C}_2\text{--C}_5$ is >70%. Rise and decay characteristics are attributable to a partial dissolution of volatile components in a dibutylphthalate trap installed to collect higher hydrocarbons.

CaO/ZSM-5 at 400 °C. Retention of bromide within the second packed bed under these conditions is better than 99.9%, with an oxide utilization of approximately 50%. The composition of the products is very similar to that observed for MeOH coupling over Ca exchanged ZSM-5 [24].

After more than 10 runs and regenerations (525 °C, 5 h, 5 sccm O_2 , quantitative Br_2 recovery), the coupling/neutralization reactivity and product distribution of the regenerated solid (50% selectivity to $\text{C}_2\text{--C}_6$) remained unchanged within experimental uncertainty. Fig. 5 shows the product output of five such run/regeneration cycles under conditions of tenfold higher flow (5 sccm CH_3Br , 45 sccm CH_4) and slightly higher temperature (450 °C) than shown in Fig. 4. In this case the solid tested had already been through 10 cycles of reaction/regeneration prior to the “first run”. Again, each run corresponds to approximately 50% of the neutralization capacity of the calcium within the composite. Although there is some time dependence to the conversion (100% early to >92% late) and product distribution within each run, the run-to-run reproducibility is high. The run-to-run variations are due to differences in timing between onset of flow and stream sampling (data not shown). Furthermore, these materials are also catalytic (Eq. (5)) in that, even after HBr breakthrough due to metal oxide depletion, the conversion of $\text{CH}_x\text{Br}_{4-x}$ under the conditions shown in Fig. 4 continues [25]. This catalytic coupling reactivity allows use of more specialized auxiliary metal oxides for HBr sequestration and Br_2 recovery.



Methane partial oxidation by free radical bromination leads to significant buildup of CH_2Br_2 and of some CHBr_3 at appreciable methane conversion. Over CaO/ZSM-5 , CH_2Br_2

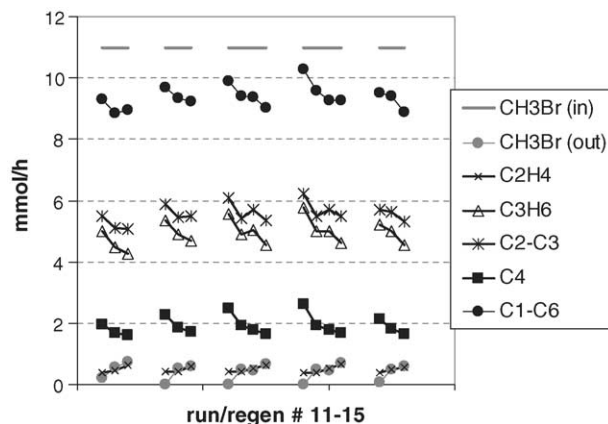


Fig. 5. Stability of CaO/ZSM-5 (10 mm $\times$ 100 mm plug, 5 g, previously cycled nine times to similar state of bromination) in reactivity for CH_3Br condensation/neutralization to olefins. Feed, $\text{CH}_4:\text{CH}_3\text{Br}$ (45:5 sccm); space time = 2 s, WHSV = 0.22 h^{-1} . Selectivity to $\text{C}_2\text{--C}_6$ is >85%. Between each run, the bed is regenerated with a flow of O_2 (2.5 sccm) for 2 h, $T = 525$ °C) and the Br_2 trapped and quantified.

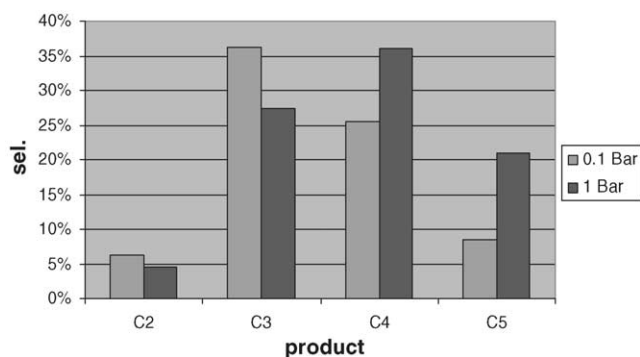


Fig. 6. CH₃Br coupling product distribution as a function of CH₃Br partial pressure (conditions as in Fig. 4 except space time for both pressures = 2 s).

condenses predominantly to adsorbed carbon in the absence of CH₃Br while cross coupling between CH₂Br₂ and CH₃Br is manifest in the higher output of aromatics (best represented as mesitylene C₉H₁₂), when both species are present [23]. As shown above, with pure CH₃Br feed, the yield of C₂–C₅ (75%) is significantly higher than observed (50%) using a mixture with significant CH₂Br₂ content (8:2 CH₃Br:CH₂Br₂). In many cases it would be advantageous to be able to tune the coupling distribution to higher hydrocarbons. Fig. 6 shows the hydrocarbon distribution may be made significantly “heavier” simply by increasing the CH₃Br feed pressure. Similar upgrading may be accomplished by lowering the coupling temperature to 325 °C as well [25].

3. Summary

The use of solid metal bromide/metal oxide pairs of reversible composition has been presented as a general scheme for partial oxidation of alkanes. The metal bromide reacts in facile fashion with oxygen to release bromine. The bromine thus formed reacts relatively selectively (compared to O₂) to oxidize C–H bonds and form HBr and C–Br functionality. The metal oxides formed in the first step in this cycle then scavenge the bromide from these halocarbon intermediate to give the oxidized product, whose specific identity may be tuned through judicious modification of the solid composition.

The advantage of Br₂ over other halogens in this partial oxidation scheme may be understood in terms of the reduction potential of Br₂ to Br[−] (1.07 V versus NHE), which in comparison with Cl₂ (1.36 V) and I₂ (0.54 V), makes alkane bromination significantly less exothermic than chlorination, yet spontaneous enough to go to completion. Bromine also allows for utilization of a wider range of metal oxides as bromide metathesis reagents because the reoxidation of metal bromides by O₂ (1.23 V) can be accomplished under relatively mild conditions.

For reactions involving methane, despite the slightly lower selectivity for monobromination versus monochloro-

ination for comparable methane conversion, a higher degree of reversibility is expected for the weaker C–Br bonds [26] than exists for C–Cl bonds for corresponding C₁ species. In addition, CH₃Br and CH₂Br₂ are expected to be significantly easier to separate from each other than are CH₃Cl and CH₂Cl₂. Hence, polybrominated methanes are not necessarily lost from a methane conversion process and may be induced to disproportionate with CH₄ feed, raising overall CH₃Br, and ultimately olefin, yield [23]. We direct further work in methane activation towards establishing the generality of the condensation reactivity of CH₃Br over microporous solids to give olefins or other products and draw on analogies to CH₃OH coupling [24].

Ultimately our goal is to utilize the three-step low temperature route – bromination, metathesis, regeneration – to streamline the production of partially oxidized higher value hydrocarbon products from alkane feedstocks. Both a better mechanistic understanding and further materials discovery for more selective halogenation and metathesis reactions continue to be key areas for further research.

4. Experimental

Supported Co and Cu oxides were prepared by sol–gel techniques as previously described. CaO/ZSM-5 composites were prepared by wet impregnation of one part Ca(NO₃)₂ to four parts H-ZSM-5, (Si:Al = 80:1, obtained from Zeolyst Corp.), drying at 125 °C overnight, followed by calcination at 500 °C overnight. Catalytic coupling reactivity was not evident until after the first CH₃Br/HBr metathesis/regeneration cycle. Nitrogen, helium, oxygen, methane, and ethane flows were controlled by mass flow control (Matheson). Bromine was dispensed by passing reactant gases through a temperature-controlled glass bromine bubbler. Methyl bromide flow was controlled by the use of capillary PTFE restrictor tubing together with a cooling bath to control the CH₃Br cylinder vapor pressure. Gas flow through multiple reactors was controlled by PTFE restrictor tubing. Care was taken to ensure the pressure drop across the restrictor was more than 10 times the pressure drop across the reactive bed. All bromine containing streams were handled with tubing/fittings made from PTFE, CTFE (Chemint/Vici-Valco), or glass. High temperature reactors were made from pyrex tubing with glass wool plugs and heated with aluminum blocks controlled with Omega thermocouples, cartridge heaters and temperature programmers. Gas analysis was performed on an HP-Plot-Q column using an Agilent 6890 GC with either TCD, FID, or MS detection.

Acknowledgements

This research was funded by Gas Reaction Technologies, Inc., through a sponsored research agreement with the University of California, Santa Barbara (PCF and GDS PI's).

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