

Self-Sustaining Smoldering Combustion: A Novel Remediation Process for Non-Aqueous-Phase Liquids in Porous Media

C. SWITZER, P. PIRONI, J.I. GERHARD,*
G. REIN, AND J.L. TORERO

Department of Civil and Environmental Engineering,
University of Western Ontario, London, Ontario N6A 5B9,
Canada, and Institute for Infrastructure and Environment,
School of Engineering, University of Edinburgh, Edinburgh
EH9 3JL, United Kingdom

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Smoldering combustion, the slow burning process associated typically with porous solids (e.g., charcoal), is here proposed as a novel remediation approach for nonaqueous phase liquids (NAPLs) embedded in porous media. Several one-dimensional vertical smoldering experiments are conducted on quartz sand containing fresh coal tar at an initial concentration of 71 000 mg/kg (approximately 25% saturation) and employing an upward darcy air flux of 4.25 cm/s. Following a short-duration energy input to achieve ignition at the lower boundary, a self-sustaining combustion front is observed to propagate upward at 1.3×10^{-2} cm/s. The process is self-sustaining because the energy released during NAPL smoldering is efficiently trapped and recirculated by the soil matrix, preheating the NAPL ahead of the reaction front. The smoldering process is observed to self-terminate when all of the NAPL is destroyed or when the oxygen source is removed. Pre- and post-soil analysis revealed that NAPL smoldering reduced the concentration of total extractable petroleum hydrocarbons (TPH) from 38 000 mg/kg to below detection limits (<0.1 mg/kg) throughout the majority of the column. A comparable experiment in which conductive heating is applied in the absence of smoldering demonstrates a 6-fold reduction in the net energy in the system and residual TPH values of 2000–35 000 mg/kg. A further repeat in which the air supply is prematurely terminated demonstrated that the NAPL smoldering process can be extinguished via external control. A suite of 23 demonstration experiments shows that NAPL smoldering is successful across a range of soil types (including simple layered systems) and contaminants (including laboratory mixtures of dodecane, DCA/grease, TCE/oil, vegetable oil, crude oil, and mineral oil) as well as field-obtained samples of materials containing coal tar, oil drill cutting waste, and oil sands.

Introduction

Tens of thousands of sites worldwide exhibit contamination of groundwater and surface water by historical and continuing accidental releases of hazardous nonaqueous phase liquids (NAPLs). Common NAPLs include petroleum hydrocarbons

(oils, fuels), polychlorinated biphenyls (electrical transformer oils), chlorinated ethenes (solvents, degreasers), creosote (wood treaters), and coal tar (manufactured gas plants). Complex and/or long-chain compounds, such as heavy oils, PCB oils, and coal tar, are particularly recalcitrant, resisting degradation via physical (e.g., volatilization), biological (e.g., dehalogenation), and chemical (e.g., oxidation) treatments that are becoming accepted remedies for more amenable contaminants. Dealing with such wastes involves excavation and either disposal to a hazardous waste landfill or incineration at substantial cost. As an alternative, this research paper proposes a new approach, NAPL smoldering, as a potential remediation process.

Combustion is the exothermic oxidation of a fuel. In the case of a carbon-based compound, the products are primarily carbon dioxide, water, and energy. Indeed, the combustibility of NAPLs is a characteristic that has been successfully exploited through the ex situ incineration of NAPLs and contaminated soil (1). Incineration is achieved primarily via flaming combustion. Flaming combustion involves the gasification of a fuel and its exothermic oxidation in the gas phase. Incineration of NAPLs by flaming combustion is energy inefficient (i.e., high heat losses); as a result, incineration requires the continuous addition of fuel and, often, supplemental energy.

Smoldering combustion, in contrast, is the exothermic oxidation of a condensed phase (i.e., solid or liquid) occurring on the fuel surface (2). Smoldering is limited by the rate of oxygen-transport to the fuel's surface, resulting in a slower and lower temperature reaction than flaming. Importantly, smoldering can be self-sustaining (i.e., no energy input required after ignition) when the fuel is (or is embedded in) a porous medium. Self-sustaining smoldering occurs because the solid acts as an energy sink and then feeds that energy back into the unburnt fuel, creating a very energy efficient reaction (1). Solid porous fuels such as polyurethane foam (3), cellulose (2), and charcoal are typical media that exhibit self-sustained smoldering. For these materials, studies have demonstrated that the rate of propagation of the combustion front and net heat generated are affected by the velocity (magnitude and direction) of air flow, pore diameter of the medium, and the fraction of porosity occupied by fuel, air, and nonreacting materials (4). Smoldering reactions can leave a carbon-based residue (oxygen limited reactions) or can result in complete combustion of the fuel (fuel limited reactions) (5). The former is common in combustible porous media where the char minimizes heat losses and enables the reaction to propagate. The latter is common when the fuel is combined with an inert porous media that provides the required insulation even in the fuel's absence.

While most research focuses on smoldering of solid fuels, there are several examples of combustion of a liquid fuel embedded in a porous matrix. Lagging fires occur inside porous insulating materials soaked in oils and other self-igniting liquids (6). To enhance oil recovery, combustion fronts are initiated in petroleum reservoirs to drive oil toward extraction points (7). The reactions involved in enhanced oil recovery through in situ combustion are described as heterogeneous gas–solid and gas–liquid between oxygen and the heavy oil residue (8). To the best of the authors' knowledge, there is no work published on the mechanisms governing the smoldering of liquids and none involving smoldering as a remediation technique.

NAPL smoldering is different from existing thermal remediation techniques. In situ thermal remediation requires the continuous input of energy in order to primarily volatilize

* Corresponding author telephone: (519) 661-4154; fax: (519) 661-3942; e-mail: jgerhard@eng.uwo.ca.

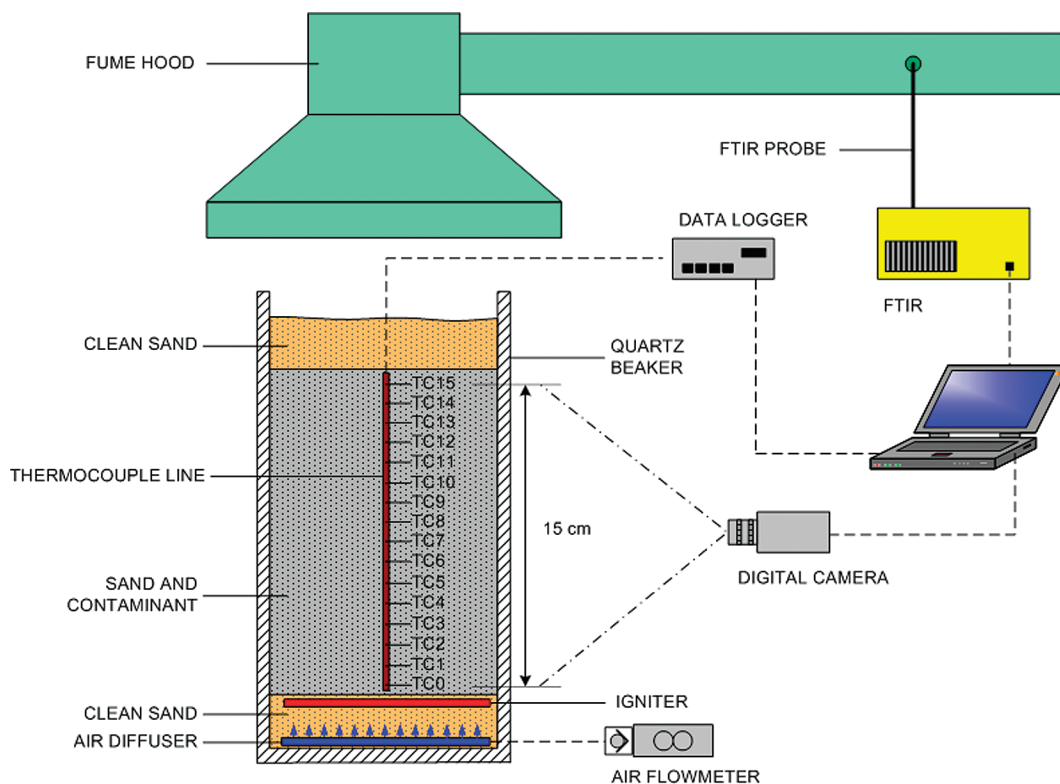


FIGURE 1. Schematic of the experimental apparatus and setup (not to scale).

and, in some cases, thermally degrade (pyrolyze) and mobilize (via viscosity reductions) the organic phase. All of these processes are endothermic and remediation continues as long as externally supplied energy input is sustained throughout the NAPL-occupied porous medium. In contrast, NAPL smoldering has the potential to create a combustion front that (i) initiates at a single location with the NAPL-occupied porous medium, (ii) initiates with a one-time, short-duration energy input, (iii) propagates through the NAPL-occupied medium in a self-sustained manner, and (iv) destroys the NAPL wherever the front passes. NAPL smoldering is different from in situ combustion for enhanced oil recovery in that the latter is designed to generate heat and pressure that will mobilize the entrapped oil toward recovery wells. NAPL smoldering, in contrast, may benefit from avoiding the recovery (and thus treatment) of NAPL and/or water.

This work presents the first experiments of liquid smoldering in the context of NAPL destruction within porous media. A base case experiment is described in detail to illustrate the viability of the process, fate of the compounds and controllability of the smoldering process in the context of coal tar remediation. A series of 23 experiments is presented to examine the potential of the process across a range of NAPL contaminants, porous media types, and other relevant parameters.

Experimental Methodology

A schematic diagram of the experimental apparatus is presented in Figure 1. Upward smoldering combustion tests were carried out in a quartz glass column 138 mm in diameter and 275 mm in height. Commercial grade fresh coal tar was employed (Alfa Aesar, Heysham, UK) in the base case, with an assumed density of 1200 kg/m³ at room temperature (9). The base case employed commercially available quartz sand (Leighton Buzzard 8/16 sand, WBB Minerals, U.K.), characterized by a bulk density of 1700 kg/m³, a mean grain size of 1.34 mm and a coefficient of uniformity of 1.35. When dry packed, the average porosity of the sand is 40%. To prepare

the contaminated material, NAPL and sand were mixed in a mass ratio corresponding to a desired (approximate) saturation (S_N , defined as the volume fraction of pore space occupied by NAPL). The target saturation for the base case was 25%, corresponding to 71 000 mg of coal tar per kg of sand. The batch was homogenized by mechanical mixing prior to packing in the apparatus.

The apparatus was packed each time in a standard sequence (Figure 1). A 30 mm layer of clean sand was emplaced followed by the air diffuser, which consisted of eight perforated 6 mm tubes radiating from a central support connected to an air compressor via an air inlet tube. Clean sand was used to bury the air diffuser by a few millimeters, upon which was emplaced the igniter: a 3.25 mm square cross section \times 762 mm length inconel-sheathed cable heater (240 V, 450 W, Watlow Ltd., U.K.) formed into a flat spiral of 130 mm maximum external diameter. The igniter was placed at the bottom and upward propagation was chosen because buoyancy favors forward propagation (3) (i.e., combustion front progressing in the same direction as the oxidizer flow). A 150 mm layer of the NAPL-contaminated sand was then emplaced. The high viscosity and cohesion of the material ensured no distinct layering or grain size separation occurred during emplacement. A final 30 mm layer of clean sand was emplaced at the top of the sample.

Fifteen 1.5 mm \times 0.5 m inconel-sheathed type K thermocouples were inserted into the sand pack along the column central axis and spaced at 10 mm intervals above the cable heater. The thermocouples were connected to a data acquisition system (Multifunction Switch/Measure Unit 34980A, Agilent Technologies). Continuous exit gas analysis was performed using a Fourier Transform Infrared (FTIR) system equipped with an onboard oxygen sensor (Analyzer Dx-4000, Gasmet Technologies).

At the start of each experiment, the material adjacent to the igniter (as measured at the second lowest thermocouple, TC1) was preheated to 400 °C, requiring approximately 90

min. on average. Once this temperature was achieved at TC1, air injection at the predetermined level (4.25 cm/s for the base case) was initiated and maintained until the end of the experiment. The igniter was turned off when the temperature at TC1 began to decrease with time (i.e., postpeak), typically a short time (e.g., 10 min) after initiating the air flow. The maximum power used for these experiments was approximately 390 W, which corresponds to a heat flux of 26 kW/m² over the horizontal cross-sectional area of beaker. This ignition protocol was determined from a series of proof of concept experiments (10).

The rate of smolder propagation was obtained from the temperature histories of the thermocouples embedded in the sand pack. The smoldering velocity was calculated from the time lapse of the front arrival at two consecutive thermocouples and the known distance between thermocouples. The front arrival at a thermocouple location was taken as the average of the times at which the temperature reached 500, 600, and 700 °C, all of which are above the observed ignition temperature (10).

Pre- and post-treatment analysis of the samples was conducted to assess contaminant destruction as an indication of the remediation efficacy. Accelerated solvent extraction (ASE) with a 50 mL mixture of dichloromethane and acetone was conducted on 20 g soil samples. The extract was analyzed for total extractable petroleum hydrocarbons (TPH) in the C₁₀ to C₄₀ range by a gas chromatograph equipped with flame ionization detector (Finnegan Focus GC, Thermo Electron Corporation, Hemel Hempstead, U.K.) and for polycyclic aromatic hydrocarbons (PAHs) by gas chromatograph equipped with mass spectrometer (Thermo Quest Trace GC and Finnegan Trace MS, Thermo Electron Corporation, Hemel Hempstead, UK).

A second experimental apparatus was employed to obtain basic smoldering data over a wide variety of test conditions more rapidly than the base case system. These demonstration experiments were conducted in a similar manner with a smaller quartz beaker (100 mm diameter). The height of the contaminated soil pack was 50 mm instrumented with 5 thermocouples. While not sufficient to give detailed smoldering data, this setup proved successful for evaluating NAPL/sol combinations that will smolder successfully.

Demonstration experiments 1–7 examined the effects of contaminant concentration. Experiment 1 represents the base case of 71 000 mg/kg coal tar in coarse sand in the smaller apparatus. In experiments 2–6, the initial coal tar concentration was varied from 14 200 mg/kg coal tar ($S_N \approx 5\%$) to 284 000 mg/kg ($S_N \approx 100\%$). In demonstration experiment 7, a mixture of 71 000 mg/kg coal tar, 100 000 mg/kg water, and coarse sand was prepared ($S_N \approx 25\%$ and $S_W \approx 40\%$).

The effects of contaminant type were examined in experiments 8–14. The NAPLs studied were mineral oil (GTX 15W-40, Castrol UK Ltd., Swindon, UK), crude oil (Nynas, Dundee, U.K.), vegetable oil (Sainsbury's, London, U.K.), dodecane (Acros Organics, Geel, Belgium), 25% grease in dichloroethane (Acros Organics), and 25% vegetable oil in trichloroethylene (Acros Organics). In experiment 14, a coal tar extracted from a former manufactured gas plant (MPG) contaminated soil (Site 1, Scotland) was tested in a medium sand (Lochaline A, Tilcon Ltd., Manchester, U.K.; mean grain size of 0.53 mm).

Demonstration experiments 15–18 examined the effects of soil type and layering. In experiment 15, medium sand was employed at a concentration of 71 000 mg/kg coal tar. In experiment 16, natural peat (excavated from a site near Edinburgh, U.K.) was mixed with coal tar at 280 000 mg/kg. In experiment 17, the apparatus was packed in two layers of equal thickness, with the coarse sand (71 000 mg/kg coal tar) overlying the medium sand (71 000 mg/kg coal tar) (see Figure S-1 in the Supporting Information). In experiment 18,

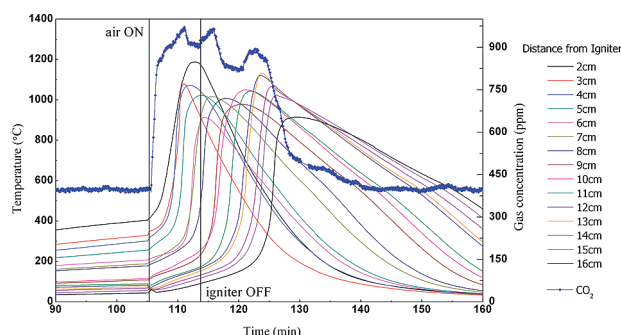


FIGURE 2. Temperature histories along the sample center axis for the base case experiment (coal tar concentration of 71 000 mg/kg, $S_N \approx 25\%$ and air flux of 4.25 cm/s).

a 1 cm layer of clean medium sand separated 2 coarse sand layers, each exhibiting 71 000 mg/kg coal tar (see Figure S-2 in the Supporting Information).

Field-contaminated samples were studied in demonstration experiments 19–23. These samples were tested as received (i.e., not dewatered). Experiment 19 employed pulverized oil sands. Experiments 20–23 were coal tar-contaminated soil samples extracted from three distinct former MPG sites in Scotland. In each case, the soil was a heterogeneous sample of “made ground” (i.e., artificial fill with wide assortment of materials from silt to gravel). Experiment 23 employed oil drilling cutting waste mixed at a 3:1 ratio with coarse sand.

Results and Discussion

Base Case Experiment. Smoldering Combustion Temperature Profiles. Figure 2 presents the evolving temperature profiles of the base case experiment (coal tar at 71 000 mg/kg). With the ignition heater initiated at $t = 0$, the temperature immediately adjacent to the igniter achieved 400 °C in approximately 105 min. The introduction of air at this time resulted in an immediate change in the rate of temperature increase, corresponding to ignition. Initiation of smoldering combustion of the coal tar at this time is confirmed by the appearance of carbon dioxide (CO₂), a combustion product, in the effluent gas stream (Figure 2, right axis). The temperature near the igniter achieved a maximum of approximately 1190 °C at 112 min (i.e., 8 min after ignition). The temperature at this location then decreased as the contaminant (fuel) was consumed by the smoldering reaction, reaching ambient temperature after approximately 160 min.

At the time of ignition, Figure 2 illustrates that the temperatures throughout the column ranged from approximately 360 °C (1 cm from the igniter) to ambient at the top of the contaminated sandpack. The power supplied to the igniter was turned off at 114 min. The energy supplied by the combustion reaction was sufficient to allow propagation of the reaction along the entire length of the contaminated sandpack. A continuous succession of nondiminishing peak temperatures (here approximately 1050 °C) in the absence of externally provided energy is characteristic of a self-sustaining smoldering process (11).

The smoldering velocity was calculated to be 1.3×10^{-2} cm/s (0.84 cm/min), a value consistent with other smoldering applications (12). Moreover, these types of temperature profiles are typical of smoldering combustion in other materials (e.g., polyurethane foam), although the observed temperatures in those materials are lower (3, 13). Coal tar is a flammable substance in the absence of porous media. The ability of the porous media to trap and recirculate the heat produced by the smoldering reaction may enhance the reaction temperatures. This effect is observed in porous

media burners, which can extend the flammability range of fuels and result in weakly flammable substances burning quite readily and even the attainment of superadiabatic flame temperatures (14–17).

Comparison to Clean Sandpack Experiment. A comparison experiment was conducted with conductive heating only applied to a sandpack with no coal tar present. In this blank experiment, the heater was left on throughout. The temperature profiles at 10 cm from the igniter in both the base case and blank experiments were compared to determine the net energy input (see Figure S-3 in the Supporting Information). The blank experiment achieved only 100 °C with constant heating, while the base case experiment achieved 1050 °C. The area under each temperature curve represents the energy accumulated at this location. Integrating the temperature profiles for the entire sandpack for both experiments quantifies the net energy input (i.e., input minus losses); this calculation reveals that the net energy input is approximately 6 times greater in the base case than the blank experiment. This difference underscores that smoldering coal tar combustion is a strong, exothermic, self-sustaining reaction.

Soil Alterations. Visual inspection of the post-treatment sand showed no apparent signs (i.e., via sight, smell, or touch) of remaining contamination throughout the sand pack (see Figure S-4 in the Supporting Information). However, the color of the sand grains had changed from yellow to red. Similar effects are observed in soils after wildfires and slash-and-burn conversion of forest land for agricultural purposes and has been correlated to fire severity (14, 15). Severe fires have been associated with water repellancy and a number of other physical and chemical changes to the soil itself (15–17); some of these changes may be reversible if addressed directly (16). More research is necessary to understand the effects of smoldering combustion on soil properties.

Comparison to Conductive Heating Alone. A repeat of the base case experiment, with coal tar concentration at 71 000 mg/kg ($S_N \approx 25\%$) was performed with conductive heating alone (i.e., no air injection). The same heating protocol was followed as the base case except that the power input was held constant instead of being terminated at 114 min. Similar heating of the two contaminated soil packs was observed initially, with 400 °C reached at the nearest thermocouple in approximately the same time in both the base case (Figure 2) and the conductive heating case (see Figure S-5 in the Supporting Information). In the absence of air injection, the temperature continued to increase slowly in the conductive heating experiment with a maximum temperature of approximately 650 °C achieved in 164 min. Maximum temperatures decreased with increasing distance from the heater, with temperatures near the top of the contaminated soil pack (12–16 cm) reaching 100 °C at the time that the power supplied to the heater was terminated. CO₂ monitoring throughout this experiment revealed that combustion was not occurring at any time (data not shown). Thus, the higher temperatures obtained in this case as compared to the blank experiment are due not to exothermic chemical reactions but mainly to the sustained high temperature at the heater for the duration of the experiment and the significantly higher heat capacity of coal tar relative to sand. This experiment underscores that smoldering combustion is a reaction that cannot proceed in the absence of an oxidant.

Terminating the Reaction. Smoldering fires of peat and coal in the natural environment have been known to burn for months or years (18, 19) because of the extensive supply of fuel, the availability of oxygen, and the self-sustaining nature of the process. To investigate the ability to control NAPL smoldering in the laboratory, an experiment was conducted under similar conditions as the base case except the air injection was terminated prior to completion. Tem-

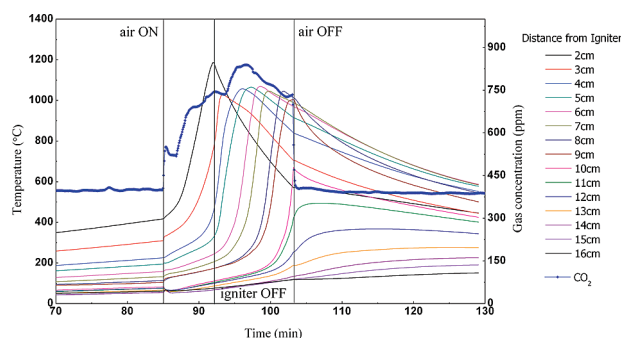


FIGURE 3. Temperature histories along the sample center axis for a repeat of the base case experiment (coal tar concentration of 71 000 mg/kg, $S_N \approx 25\%$ and air flux of 4.25 cm/s) in which the air supply was terminated prematurely.

TABLE 1. Summary of Chemical Analysis Results

distance from igniter (cm)	base case		heat only		terminated	
	TPH (mg/kg)	PAH (mg/kg)	TPH (mg/kg)	PAH (mg/kg)	TPH (mg/kg)	PAH (mg/kg)
0–1	<0.1	<0.1			580	
1–2	<0.1	<0.1	2210	680	760	730
2–3	<0.1	<0.1			330	
3–4	<0.1	<0.1	11800	5370	450	430
4–5	0.3	0.3			500	
5–6	<0.1	<0.1	29300	14100	190	170
6–7	<0.1	<0.1			980	
7–8	<0.1	<0.1			580	
8–9	<0.1	<0.1			6150	
9–10	<0.1	<0.1	33900	7730	3080	2030
10–11	<0.1	<0.1			7650	
11–12	<0.1	<0.1			36200	
12–13	1.2	1.2			42000	
13–14	<0.1	<0.1	35000	9500	29500	27800
14–15	<0.1	<0.1			30800	
15–16	<0.1	<0.1			30600	

perature profiles in this case followed similar trends to the base case until the air was terminated (Figure 3). Near the bottom of the contaminated sandpack, where the smoldering reaction may have reached completion, the temperature profiles are relatively undisturbed by the termination of the air flow (except for a decrease in the rate of temperature reduction due to the loss of the cooling effect). In the center of the sandpack, where increasing temperatures suggested that the smoldering reaction was beginning, the temperatures decreased rapidly after air termination. This shift suggests that for the fuel and conditions examined here, the smoldering reaction cannot sustain itself in the absence of supplied air, which is confirmed by the immediate reduction in CO₂ back to ambient levels (Figure 3). Termination experiments were conducted for a number of different conditions with identical results; the reaction did not continue in the absence of an externally supplied air flow.

Fate of Coal Tar Compounds. *Chemical Analysis of Post-Treatment Soil.* Chemical analysis was conducted on spatially sequential subsamples of the post-treatment sands in the three coal tar-contaminated experiments: base case, conductive heating only, and air supply terminated. Prior to the experiments, the base case coal tar sand packs exhibited TPH of approximately 38 000 mg/kg in the C₁₀ to C₄₀ range (71 000 mg coal tar/kg sand as prepared, $S_N \approx 25\%$) and PAH content of approximately 9500 mg/kg. Postexperiment, the base case revealed no measurable TPH or PAH (i.e., below detection limit of 0.1 mg/kg) in the majority of locations (Table 1). The top of the initially-contaminated sandpack exhibited the highest residual TPH value of 1.2 mg/kg, likely

TABLE 2. Demonstration Experiments Conducted Across a Range of Conditions

	Experiment	Porous Media	Contaminant	concentration (mg/kg (S _N))	ignition temp (°C)	max. temp (°C)	time to ignition (min)	air flow rate (cm/s)	propagation velocity (m/s)	Comments
saturation	1	coarse sand	coal tar	71000 (25%)	400	1010	50	4.25	1.40E-04	Base case experiment at a smaller scale.
	2	coarse sand	coal tar	280000 (100%)	400	1178	80	4.25	1.12E-04	
	3	coarse sand	coal tar	230000 (80%)	400	1277	80	4.25	2.00E-04	
	4	coarse sand	coal tar	140000 (50%)	400	1045	85	4.25	1.02E-04	
	5	coarse sand	coal tar	28000 (10%)	400	784	50	4.25		Not self-sustaining. Centre is clean but contamination is apparent near edges.
	6	coarse sand	coal tar	14000 (5%)	400	578	45	4.25		Not self-sustaining. Centre is clean but contamination is apparent near edges, more severe than experiment 5.
	7	coarse sand	coal tar water	71000 (25%) 100000 (100%)	470	1040	47	5.31	7.40E-05	Faster ignition than base case but slower propagation.
contaminant	8	coarse sand	mineral oil	210000 (near 100%)	400	890	23	4.25		Successful ignition.
	9	coarse sand	crude oil	210000 (near 100%)	400	705	53	4.25		Successful ignition.
	10	coarse sand	vegetable oil	210000 (near 100%)	203	786	44	4.25		Successful ignition.
	11	coarse sand	dodecane	180000 (near 100%)	240	660	32	4.25		Successful ignition.
	12	coarse sand	DCA/grease	290000 (near 100%)	200	688	22	4.25		75% / 25% mass ratio of DCA to grease. Successful ignition.
	13	coarse sand	TCE/oil	340000 (near 100%)	350	689	24	4.25		75% / 25% mass ratio of TCE to oil. Successful ignition.
	14	medium sand	field coal tar 1	unknown	250	1053	52	4.25	9.80E-05	Coal tar from same site as experiment 20 mixed with medium sand in the laboratory.
porous media	15	medium sand	coal tar	71000	400	822	23	5.31	1.40E-05	Faster ignition than base case but slower propagation.
	16	peat	coal tar	280000	300	1010	47	5.31	3.50E-05	Peat from a site near Edinburgh, U.K. mixed with laboratory coal tar. Self-sustaining smouldering, but peat destroyed, too.
	17	2 layers -coarse over medium sand	coal tar	71000	425	1139	43	4.25	8.30E-05	Coal tar mixed with coarse sand (71,000 mg/kg) above coal tar mixed with fine sand (71,000 mg/kg).
	18	3 sand layers (middle layer clean)	coal tar	71000	400	1139	47	4.25	8.30E-05	1cm layer of clean medium sand separating two layers of coal tar in coarse sand (71,000 mg/kg).
field materials	19	oil sands	petroleum solids	unknown	300	1066	35	4.25	1.70E-04	Oil sands of North American origin. Initial fused material pulverised prior to STAR test. Post-treatment material similar to the clean medium sand.
	20	made ground 1	field coal tar 1	unknown	400	1104	72	4.25	5.30E-05	Post-treatment material is mainly fine grain with some small aggregates.
	21	made ground 2	field coal tar 2	65000	400	795	90	4.25		Initial concentration determined by loss on ignition. Strong ignition. Possible self-sustaining smouldering (longer sample needed to verify).
	22	made ground 3	field coal tar 3	12000	400		75	4.25		Initial concentration determined by TPH and loss on ignition methods. Weak ignition observed.
	23	oil drill cutting waste	residual crude oil	unknown	415	538	70	4.5		Drill cuttings diluted with coarse sand (3:1). Successful ignition and propagation observed, but peak temperatures decayed over time.

related to the condensation and deposition of volatile components or combustion products. At the same subsampling intervals, conductive heating alone was observed to reduce the coal tar concentrations significantly close to the heater (e.g., 2210 mg/kg) and residual TPH concentrations increased with increasing distance (Table 1; see Figure S-6 in the Supporting Information). Residual TPH values are observed to increase with decreasing maximum temperature achieved during the experiment. The absence of vapor or liquid extraction to remove the coal tar suggests that conductive heating alone mobilized the coal tar, possibly below the heater and the air diffuser where subsampling was not conducted. In the termination experiment, residual TPH values increased as distance from the igniter increased (Table 1). Locations near the igniter did not exhibit TPH reductions as significant as the base case experiment, suggesting that despite being well along in the cooling stage, continued smoldering may have been interrupted by air termination.

Characterization of Emissions. Emissions characterization was conducted by real-time FTIR analysis of the exhaust gas stream. The significant gaseous products were carbon dioxide, carbon monoxide and naphthalene, with maximum concentrations of 2100, 430, and 56 ppm, respectively. Trace amounts of toluene and *m*-xylene were identified in the exiting gas stream (maximum concentration of 15 ppm). Methane and hexane were also measured in trace quantities in amounts too low to quantify. Nitrogen and sulfur oxides were not detected above the threshold value of 1 ppm. In general, emissions are anticipated to be a function of the contaminant, the soil, and the operating conditions. Further emissions analysis is warranted across a range of contaminant and soil conditions to facilitate their control or capture.

Gaseous Byproduct Formation. Because NAPL smoldering involves the combustion of hazardous materials, the potential

exists for the formation of harmful byproducts during the smoldering process. Chemical compounds such as polychlorinated dibenzo dioxins and furans (PCDD/Fs) have been reported in the context of municipal solid waste (MSW) incineration (20, 21). Optimal conditions for PCDD/F formation may include (i) temperatures of 200–400 °C (21, 22), (ii) significant chlorine content in the starting material (22–24), and (iii) the presence of catalysts such as copper or iron (22). At temperatures greater than 400 °C, PCDD/Fs tend to undergo thermal decomposition (21). A standard protocol for post-treatment of incinerated MSW to remove PCDD/Fs is thermal treatment at greater than 850 °C for more than 2 s (22). In addition, the presence of sulfur either in the waste material itself or as an additive during the combustion process may inhibit PCDD/F formation (24, 25).

These factors suggest that smoldering combustion of coal tar, in which the physical processes differ substantially from traditional incineration, is not likely to produce PCDD/F compounds. Coal tars typically have little or no chlorine content. In addition, the peak temperatures observed (in excess of 1000 °C) favor PCDD/F destruction. Further, the emission of SO_x compounds, which are anticipated in the combustion of some coal tars, suggest further inhibition of PCDD/F production during coal tar smoldering. Nevertheless, direct testing is warranted to investigate the absence of harmful gaseous byproducts such as PCDD/Fs; however, gas emission volumes were expected to be too low to conduct this analysis in the presented experiments.

Demonstration Experiments. Demonstration experiments were conducted to examine the applicability of NAPL smoldering combustion across a range of typical contaminant and soil conditions, identifying important areas for future work (Table 2). In all cases, NAPL smoldering was initiated successfully and propagation was observed. In the cases

where peak temperatures do not decay with distance from the igniter (i.e., clearly self-sustaining), a propagation velocity is reported; if peak temperature decay is observed, a propagation velocity is not reported.

Initial concentration was varied in experiments 1–6. Time to ignition seemed to increase with coal tar concentration and, except for experiment 3, the smoldering propagation velocity appeared to slow with increasing concentration. Self-sustaining smoldering was not observed in experiments 5 and 6, suggesting that at these low concentrations, heat loss effects become significant. These data suggest that in the range between 28 400 and 71 000 mg/kg coal tar ($10\% < S_N < 25\%$) in this experimental system, a critical concentration exists where self-sustaining smoldering becomes possible. Because heat loss effects decrease with increasing scale (because of the reduced surface area to volume ratio), this critical concentration is expected to be lower at larger experimental scales.

In experiment 7, when coal tar (71 000 mg/kg) and water (100 000 mg/kg) were both present in coarse sand, the time to ignition appeared faster than in the base case with no water present and the peak temperatures were similar. The observed propagation velocity was slower than the base case, despite a slightly higher air flux. These phenomena are not necessarily contradictory. For ignition, conductive heat transfer is important. At the igniter, the presence of modest water contents may help to ignite the coal tar faster by acting as a heat sink helping to accumulate heat locally. At the same time, the soil moisture may slow the smoldering propagation velocity because the moisture away from the igniter continues to serve as a heat sink. At higher moisture contents, the presence of water may delay both ignition and propagation.

Experiments 8–14 varied contaminant type. All of the pure and mixed NAPLs employed exhibited ignition and propagation of the smoldering front. In all cases, except experiment 14 (field coal tar), the peak temperatures decayed with distance; however, in all cases, the final sandpack appeared clean to sight, smell, and touch. These preliminary results suggest that self-sustaining smoldering may be possible for these contaminants at a larger experimental scale.

In the experiments that varied porous media type (experiments 15–18), self-sustaining smoldering was observed in all cases and all resulted in an apparently clean sandpack. In experiment 15, ignition was achieved faster in the medium sand than the base case, but smoldering propagation was an order of magnitude slower than in the base case despite a higher air flow rate. The finer grain size may have reduced oxygen availability to the smoldering reaction, slowing propagation. In experiment 16, the peat acted as an additional fuel and both NAPL and soil were destroyed. In experiments 17 and 18, the permeability contrasts did not inhibit the continuous propagation of the smoldering front, nor did the presence of a 1 cm lens of clean material. There may be a critical thickness of clean layer, likely scale-dependent, that inhibits propagation of the reaction.

Experiments 19–23 demonstrated that successful smoldering was possible in a variety of samples obtained from NAPL-contaminated sites. Smoldering behavior seems to correlate strongly to contaminant type and initial concentration. Heavy hydrocarbons such as coal tar and the petroleum present in the oil sands may have performed best because the smoldering reactions may have been energetic enough to overcome the severe heat losses of the small demonstration system.

The smoldering combustion of liquid contaminants has been demonstrated for the first time in this work. Once ignition is achieved in samples of fresh and field-derived

coal tars, the process is observed to result in a self-sustaining reaction that propagates in the absence of additional external energy input. Under the employed laboratory conditions, NAPL smoldering achieves essentially complete elimination of coal tar. The self-sustaining reaction appears to depend on air injection and thus can be terminated at any time by the operator. The smoldering reaction self-terminates when the NAPL fuel in its path is consumed. Conductive heating in the absence of air injection did not produce combustion and resulted in much higher levels of residual contamination. Demonstration experiments suggest that smoldering combustion may be applicable across a substantial range of NAPLs and soil conditions. The results suggest that smoldering destruction of NAPLs has significant potential as a remediation approach. It may be particularly promising for soils exhibiting complex, long-chain, and/or low-volatility NAPL contamination (e.g., coal tar, heavy petrochemicals, PCB oils), where existing remediation strategies may be expensive (energy intensive), time-consuming or ineffective.

As with any technology innovation, many research questions remain to be answered. There will be limits to the applicability of the process, in terms of minimum NAPL calorific output, minimum NAPL concentration, and minimum air injection rate. The influence of other practical and site-specific factors is currently being investigated at the bench scale, including the presence of (nonfinite) thermal sinks such as water, soil heterogeneity, and organic carbon content. The scale-up of NAPL smoldering as both an ex situ technique (i.e., for excavated soils) and in situ approach (i.e., on site, avoiding excavation) is currently being researched.

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Supporting Information Available

Additional figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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