

An Innovative Ignition Method using SWCNTs and a Camera Flash

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ABSTRACT

This paper describes an ignition method that uses a simple camera flash and single-walled carbon nanotubes (SWCNTs) to ignite various fuels. This method has been used to ignite both solid and liquid fuels. The effects of iron (Fe) nanoparticles (embedded in the SWCNTs) concentration on the ignition process have been studied. The application of this nano-technology based ignition method may also be extended to achieve distributed ignition that would allow ignition in numerous locations simultaneously.

Keywords: nanotube, ignition, combustion

INTRODUCTION

Many industrial processes that utilize chemical reactions in their applications often require an initiation stimulus to start the conversion of the chemicals to desired products. A process which initiates the combustion of fuels is commonly referred to as ignition. A device which achieves this goal is a critical system component for most combustion processes especially in mobile or stationary power producing machines. For example, improper ignition during the firing of a rocket engine for lift-off can lead to combustion instability causing a catastrophic engine failure and possible loss of the spacecraft and human life, see Harrie and Reardon [1]. Also, the ignition characteristics in a gasoline-fueled automotive engine can strongly affect the fuel's burn rate, the chamber's combustion efficiency, and the exhaust emission profile.

Although many ignition methods exist, by far the most popular one is the electric spark igniter. It requires high-energy input supplied by a high-voltage circuitry often consisting of heavy components, and by its nature is a single-point stimulus method. Other ignition methods such as plasma jet injection or flame jet initiation, and high-power laser ignition are all bulky, heavy and expensive to operate. Other approaches to ignition can be through the usage of pyrophoric charges or via the mixing of hypergolic chemical components, or through activation over a catalytic bed, all of which either make use of hazardous chemicals and/or of highly specialized materials or

sophisticated mixing machinery. Again these are either single-point initiation methods, as in the case of focused-beam laser ignition, or limited to a narrowly-defined region in the combustion chamber, uncontrollable by the operator.

Another disadvantage of these ignition systems, with the exception of perhaps lasers, is that once they are installed on an engine, the ignition location remains fixed with respect to the combustion chamber. It is often preferable to have a plurality of ignition points to initiate a uniform or well-distributed combustion initiation. However, using the above-described fixed-point ignition techniques, multi-point ignition within a chamber can only be achieved by repeated implementation of the same ignition hardware, which spatially can be very restrictive to attain in addition to increasing the engine size and mass. Additionally, the ability to select and continuously vary the ignition locations or regions in an engine as a parameter, or "distributed ignition," is a critical and useful engineering design strategy for developing highly-efficient and possibly more stable combustion chambers. Current ignition methods are known to possess one or more other disadvantages such as causing combustion instability, start-up transients which not only can bring severe damage but also degradation in engine efficiency and emission of pollutants, see Harrie and Reardon [1]. Thus, an ignition method is needed which is effective, multi-point or distributed in nature, while allowing design versatility in decreasing engine size and overall mass. At the same time, such a method should exhibit increased ignition efficiency and contribute positively towards reduction of harmful pollutants.

USING SWCNTS AND A CAMERA FLASH TO IGNITE FUELS

Ajayan, et al. [2] were first to report that as-produced SWCNTs ignite when subjected to a common photographic flash at a close range. This effect was observed for dry, "fluffy" SWCNTs and was diminished somewhat for compacted material. Ignition did not occur for similar materials such as multi-walled nanotubes (MWCNTs), graphite powder, fluffy carbon soot, and C₆₀. The observed structural changes in the SWCNTs during an ignition process indicate a temperature in excess of 1500°C.

Ajayan et al. [2] explained this process through generation of a heat pulse, created through light absorption by the nanotubes, combined with inefficient heat dissipation due to the structure of the nanotubes. Braidy et al. [3] confirmed the flash ignition effect on SWCNTs but also reported the presence of iron oxide particles in the combustion byproducts. These were reported to be predominantly Fe_2O_3 with a small amount of Fe_3O_4 . The diameters of these oxide particles varied depending on their proximity to the nanotube bundles. Particles within the bundles ranged from 15 to 20 nm in diameter, while free-standing fused grains, which were not enclosed by nanotube bundles, ranged from 15 to 50 nm in diameter. The electron energy loss spectroscopy (EELS) was used to show that both types were indeed Fe_2O_3 . Both morphology types were considerably larger than the nanoparticles of Fe in the pristine SWCNTs, which were 1-5 nm in diameter. Smits et al. [4] conducted experiments to determine the cause for ignition of the SWCNTs. They tested three different samples: (a) as-produced SWCNTs synthesized by the HiPco process (from Carbon Nanotechnologies Inc.), (b) the same material obtained but after a purification process, and (c) 99.5% pure, 6 -10 μm diameter Fe powder. All three samples were subjected to identical flash lighting and subsequently micro analyzed. When flashed, both the as-produced SWCNTs and the Fe powder ignited, while the purified SWCNTs showed no reaction. Burning of the unpurified SWCNTs and Fe powder occurred slowly in small, localized locations, giving off a faint red-orange glow. The burning spread slowly, typically lasting 1-3 s before dying out. Burning of the Fe powder could be extended to several seconds by physical agitation. Examination of the nanotube samples by unaided eyes revealed relatively large clusters of hardened, orange material in the burned areas. TEM analysis of the as-produced nanotube samples before burning revealed large quantities of Fe nanoparticles 3-8 nm in diameter. The Fe particles appear to be contained within the nanotube bundles and along their exterior surfaces. After flashing the as-produced SWCNTs, the Fe nanoparticles changed from evenly-distributed throughout the sample to large clusters of particles with substantially increased diameters. The particle sizes after burning have increased from 3 to 8 nm in diameter to well over 100 nm. The structure of SWCNTs had been altered by exposure to high temperature and their diameters were no longer uniform. The large increase in particle size suggests that the Fe particles melted and coalesced which imply temperatures in excess of the melting point of Fe, or 1538°C. It seems that radiant energy transfer from the flash to the SWCNTs and the Fe nanoparticles causes different responses, and it is likely that the heat dissipates in the highly conductive and interconnected CNT bundles whereas it is almost entrapped locally in the Fe nanoparticles. The nanoparticles are also encapsulated in carbon atom layers which may serve to insulate the Fe. Catalytic Fe nanoparticles, created during the SWCNT synthesis process, with sizes on the order of

those found in the as-produced SWCNTs are highly pyrophoric with a propensity to spontaneously ignite in the presence of oxygen, resulting in oxides of iron (Fe_2O_3 and Fe_3O_4). Bare Fe nanoparticles observed on the exterior surfaces of the SWCNT bundles are most susceptible to oxidation. Sub-surface Fe nanoparticles are likely to be involved in the oxidation process as well. Chiang et al. [5] describe that the carbon shells are known to be permeable to oxygen and allow oxidation of Fe nanoparticles. The first step in the purification of SWCNTs involves the oxidation of encapsulated Fe nanoparticles. The remaining Fe nanoparticles left after the purification process are less likely to oxidize during flash exposure. Smits et al. [4] found that the exothermic oxidation of Fe released sufficient heat to cause melting, coalescence and oxidation of nanoparticles, which caused aggregation into clusters of large particles. The heat released during the oxidation is sufficient to promote transformations within the adjacent SWCNTs, including fusing some SWCNTs into larger tubes. This indicates temperatures in excess of 1500 °C. Iron melts at 1538 °C and the fully-oxidized Fe_2O_3 compound decomposes at 1565 °C, which is likely the temperature range of the reaction. In addition to structural modifications of the SWCNTs during the ignition and combustion processes, some material is reduced to an amorphous state. Amorphous carbon coatings are found on most of the Fe_2O_3 particles. These may have condensed on the surface of the Fe_2O_3 particles during cooling of the oxide particles. Smits et al. [4] believe that the flash ignition of SWCNTs should be attributed to the pyrophoric nature of fine Fe particles within the nanotube bundles, rather than to any property of the SWCNTs themselves. However, the SWCNTs are providing a medium to stabilize these nanoparticles not to spontaneously initiate ignition until they are exposed to an appropriate stimulus such as energy from an ordinary camera flash.

We have used this observation to develop an ignition method that is capable of igniting liquid hydrocarbons, such as RP-1 and methanol, and solids, such as Potassium-Chlorate (KClO_3) and wax paper with SWCNTs and a camera flash. A U.S. patent has already been applied by Chehroudi et al. [6] and is pending. A small amount (a fraction of a milligram) of SWCNTs along with a few drops of fuel could be ignited with a camera flash placed a few millimeters above the SWCNTs. The camera flash would ignite the SWCNTs in multiple locations and the heat released by the oxidizing Fe nanoparticles would ignite the fuel. As the fuel burned off, more of the SWCNTs would ignite until the entire amount was consumed. The fuel would usually burn off much faster than the SWCNTs. As the SWCNTs burned, there appeared a faint glow in the areas where it ignited first and the mixture would turn from black to an orange in color. What remained after the end of the combustion process was a much denser and harder mixture. To have a successful ignition, the SWCNTs had to be arranged in a

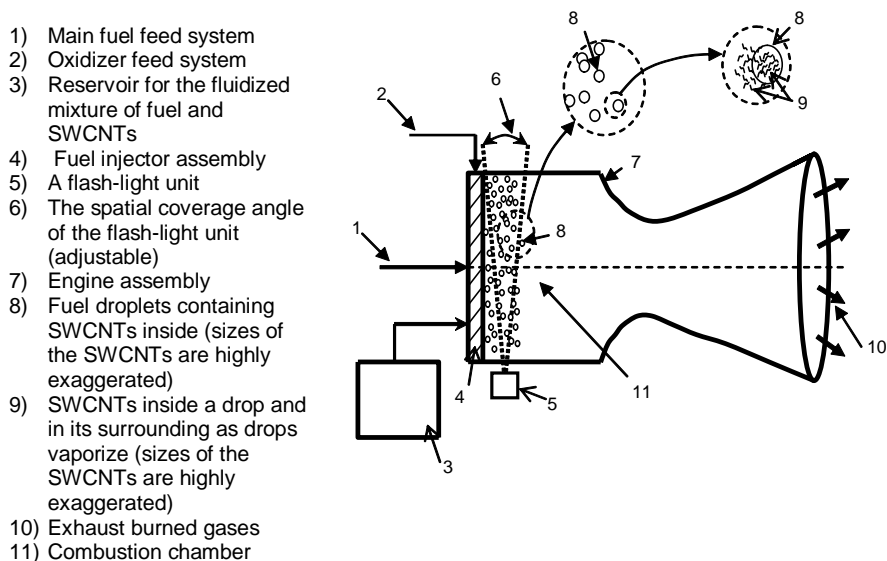


Figure 1. Ignition of a rocket engine using SWCNTs and a laser.

“fluffy” pile and as the ignition sites moved from one location to another, one could observe the pile collapsing on itself. Ignition did not occur if the pile of SWCNTs were compacted before being exposed to a flash light. There is no reason to believe that the metal oxides which remained in our tests are any different than what Brady et al. [3] and Smits et al. [4] described. The orange-colored material is most likely iron oxides Fe_2O_3 and Fe_2O_4 . The iron oxide particles that remained after our combustion were much larger than any particles that were in the initial mixture. This reinforces the observation by Smits et al. [4] that the Fe particles melted and coalesced as the oxidation continued. Since the nanosized Fe particles are pyrophoric, it is believed that the SWCNTs must stabilize the Fe particles as mentioned before. What has not yet been determined is the mechanism by which the flash either damages the SWCNTs, exposing the Fe particles to the oxygen, or somehow makes the Fe particles more reactive.

We have found that the SWCNTs were only able to ignite the fuels when the SWCNTs were in contact with the air or immersed in an oxygen-rich environment. The SWCNTs did not ignite the fuels if they were completely submerged in liquid fuels. If they were submerged completely, then only when the liquid fuel was allowed to vaporize and consequently expose the SWCNTs to sufficient oxygen, was the mixture able to be ignited with a flash.

The effects of the concentration of the Fe nanoparticles on the ignition process were also studied. As-produced SWCNTs synthesized by the HiPco process (from

Carbon Nanotechnologies Inc.) has Fe concentrations of approximately 30% by weight. These SWCNTs are very “fluffy” and reliably ignite in atmospheric air using a camera flash. Carbon Nanotechnologies Inc., also purified SWCNTs to an Fe concentration of approximately 3% by weight. Samples of these SWCNTs were much less “fluffy” than the as-produced SWCNTs. The as-produced SWCNTs occupied approximately five times the volume of the purified SWCNTs. To reliably ignite the purified SWCNTs, they had to be exposed to an oxygen-rich environment. In this case, a small amount of oxygen was flown over the sample while it was flashed. However, if the SWCNTs were purified once more to an Fe concentration of 1.5% by weight, the SWCNTs would not ignite even in an oxygen-rich environment.

The smallest amount of SWCNTs needed to reliably ignite the fuels tested here has not been established yet. In this preliminary study, we have focused on using amounts that could reasonably be assumed to exist in a single large droplet (approximately 100 μm). It is believed that as the Fe concentration in the sample is increased, the amount of SWCNTs can be decreased. It has been observed that when flashing SWCNT samples without the fuel, very small amounts of SWCNTs will ignite. These amounts are hardly visible to the naked eye and it is not unreasonable to assume that the SWCNTs could be agglomerated in such a way to minimize the amount of SWCNTs needed to reliably initiate ignition.

Figure 1 shows a concept ignition system for a rocket engine using SWCNTs and a short-duration light

source. The SWCNTs would be mixed with the fuel and as the mixture atomized forming droplets and vaporized the SWCNTs would be exposed to the oxidizer which can then be ignited with the light source. This technique could offer the ability to produce distributed ignition with multiple droplets being ignited throughout the light-exposed volume (or plane if a laser beam is used). The expanded views in the inset show the individual droplets containing SWCNTs vaporized to a sufficient level where they leave SWCNTs free to have full contact with oxidizer molecules and be ignited upon light flashes. The SWCNTs could also be injected into or fluidized with the oxidizer which would eliminate the need for droplet vaporization necessary in the previous method to expose the SWCNTs to oxidizer molecules.

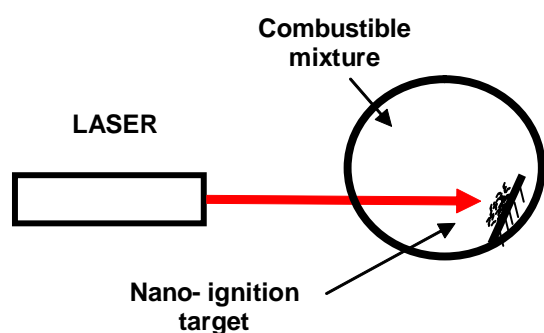


Figure 2. Laser ignition system using a target coated with SWCNTs

Figure 2 shows another low-power laser ignition conceptual design. The current laser ignition systems use a high-power laser that is focused on a metal target. The laser must have enough energy to produce a plasma cloud when the laser pulse impinges the target. This plasma then ignites the combustible mixture in the vicinity of the target causing combustion in the chamber. By using a plate coated with SWCNTs as the laser target material, one could produce a low-energy ignition system since it was shown that SWCNTs can be ignited with a laser power as low as 100 mW/cm^2 .

CONCLUSION

It has been demonstrated that SWCNTs and an ordinary camera flash can be used as an ignition source for a variety of fuels. It is believed that the Fe nanoparticles in the SWCNTs are the entities actually ignited by the flash and the burning of these Fe particles lead into the ignition of the fuels. As-produced SWCNTs with Fe concentrations of 30% by weight are reliably ignited in atmospheric air. As the Fe concentration is reduced to approximately 3% by weight, the SWCNTs must be in an oxygen-rich environment to reliably ignite. If the Fe concentration is reduced to 1.5% by weight, the SWCNTs can no longer be

ignited. The exact mechanism which causes the camera flash to ignite the Fe particles has not yet been determined. Once this mechanism is clarified, it is believed that we will be in better position to customize the SWCNTs to produce the desired ignition. Two industrial applications were briefly explained which show the exciting potential of this nano-technology based novel ignition technology.

REFERENCES

- [1] Harje, D. T. and Reardon, F. H. Liquid propellant rocket combustion instability, NASA SP-194, Scientific and Technical Information Office, Washington, D. C., 1972.
- [2] Ajayan, P.M., Terrones, M., de la Guardia, A., Hue, V., Grobert, N., Wei, B.Q., Lezec, H., Ramanath, G., Ebbesen, T.W., Science 296 (2002) 705.
- [3] Braidy, N, Botton, G. A., and Adronov, A., Nanoletters 2 (11) (2002) 1277-1280.
- [4] Smits, J., Wincheski, B., Namkung, M., Crooks, R., Louise, R., Material Science and Engineering A358 (2003) 384 -389.
- [5] Chiang, I.W., Brinson, B.E., Huang, A.Y., Willis, P.A., Bronikowski, M.J., Margrave, J.L., Smalley, R.E., Hauge, R.H., J. Phys. Chem. B 105 (2001) 8297 – 8301.
- [6] Chehroudi, B., Vaghjiani, G. L., and Ketsdever, A. Method for distributed ignition of fuels by low-energy light sources, United States Patent Office, Patent Pending, 2004.