Laser-Induced Carbon-Doped Carbonate Propellant Thermal Decomposition for Use in Beamed Energy Propulsion

Tyler R. Baxter[1]
Department of Physics & Astronomy, St. Cloud State University, St. Cloud, MN 56301

John E. Sinko[2]
Department of Physics & Astronomy, St. Cloud State University, St. Cloud, MN 56301
The Institute for Materials, Energetics, and Complexity, St. Cloud, MN 56301

Laser propulsion is an advanced propulsion technique supported by 50 years of research and development. This study develops the understanding of laser-mediated chemical propellants for beamed energy propulsion. Our immediate intent is experimentally testing space-based laser 'tractor beam' propulsion using these compounds. The suggested process would produce reversible thrust on distant macroscopic objects via confined ablation for development of a retrieval system for astronauts, space assets, or satellite deorbit. In our experiments, we irradiated pressed, carbon-doped ammonium carbonate and sodium bicarbonate powders with argon laser radiation at 514.5 nm. The sample mass was monitored in real time during each test, in order to make a first-order assessment of mass removal (gas generation) that could be used in a laser propulsion engine. A small percentage (~1%) of added carbon (graphite) dust in the pressed powder greatly enhanced mass removal from the sample. We believe these and similar materials may hold niche utility for beamed energy propulsion in sensitive operations by providing negative chemical feedback to prevent a runaway reaction that could lead to propellant explosion.

Nomenclature

c	=	Specific heat, J kg^{-1}
m	=	Ablated mass, kg
L	=	Heat of decomposition, J kg^{-1}
M^2	=	Beam parameter product
P	=	Laser beam power, W
Q	=	Heat, J
t	=	Time, s
T	=	Temperature of propellant, K
T_d	=	Thermal decomposition temperature, K
T_s	=	Sublimation temperature, K

I. Introduction

LASER propulsion is an advanced propulsion technique with about 50 years of history beginning with the work of Marx and Kantrowitz.[1,2] A number of propellant concepts have been explored during this history, ranging from metals to polymers to liquids.[3-5] In an effort to make some sense of the results, a schematic tree categorizing ablation pathways was previously outlined by Pakhomov and Sinko.[6] Separately, several authors have created analytical models of ablation which incorporated or accounted for chemical contributions to the ablation process.[7-9] We can roughly describe mass removal rate as:

[1] Undergraduate student, Dept. of Physics & Astronomy, 720 Fourth Ave. S., St. Cloud, MN 56301, Student Member.
[2] Assistant Professor, Dept. of Physics & Astronomy, 720 Fourth Ave. S., St. Cloud, MN 56301, Member.

$$\frac{dm}{dt} = \frac{1}{c\Delta T + L}\frac{dQ}{dt} = \frac{P}{c\Delta T + L} \quad (1)$$

Our focus in this paper is related, since the energy required for chemical decomposition will play a large role. Even though we are not directly vaporizing any propellant, the laser-material interaction generates gases, and the same physics should be relevant.

The second author previously proposed a cooperative 'laser tractor-beam' for the retrieval of astronauts.[10] Subsequent preliminary experimental studies of bilayer propellants demonstrated functional, switchable thrust for a single target with small numbers of pulses.[11-12] Primary attempts were made during these studies to design further complex propellant configurations, however, a suitable composite target was not achieved, for reasons due to catastrophic target damage, short mean-time-to-failure, and inconvenient options for coupling to an applicable payload. A significant challenge in this line of research is developing a propellant concept with acceptable thrust capability at 'safe' laser power levels to avoid collateral damage to equipment and spacesuits, or injury to the astronauts themselves. Confined ablation seems promising as a pathway to achieving the goals of the project. This means that chemically energetic propellants may need to be avoided to prevent a runaway scenario under confinement, which could lead to explosion of a target chamber. Specifically, if the propellant chambers are located on a space suit, a self-sustaining reaction could lead to suit rupture or even explosive decompression. One option is to intentionally select endothermic propellants with low ablation threshold; i.e. low decomposition temperatures and small activation energies. Ideally, this process would produce as many moles of gas as possible per mole of solid propellant. Thus, we decided to test propellants for which the response to strong heating is thermal decomposition, sometimes described as thermolysis. One family of such chemicals is the inorganic carbonates, which evolve carbon dioxide under heating, and in general, reducing to an oxide form. Essentially, we are making use of a reaction pathway such as $XCO_3 \rightarrow XO + CO_2$. Thus; in general, one mole of CO_2 would be evolved per mole of reactant during decomposition.

Table 1. Decomposition temperature for candidate propellants.[13,14]

Chemical Name	Chemical Formula	T_d [K]
Ammonium bicarbonate	NH_4HCO_3	309-333
Ammonium carbonate	$(NH_4)_2CO_3$	331
Potassium bicarbonate	$KHCO_3$	373-473
Copper carbonate, basic	$CuCO_3 \cdot Cu(OH)_2$	473
Silver carbonate	Ag_2CO_3	491
Sodium bicarbonate	$NaHCO_3$	543
Zinc carbonate	$ZnCO_3$	573
Manganese carbonate	$MnCO_3$	623
Magnesium carbonate	$MgCO_3$	779
Calcium carbonate	$CaCO_3$	974

An arbitrary limit of 1000 K for the threshold decomposition temperature to ensure that our laser could drive the propellant material to the target temperature. Carbonates based on mercury, lead, chromium, cadmium, and similar heavy metals were excluded due to concerns about toxicity. The remaining carbonate candidates are presented in Table 1. The information is arranged in order of increasing thermal decomposition temperature. One important point is that these decomposition temperatures may vary under reduced pressure conditions.

II. Experimental Methods and Sample Preparation

The experimental setup for this study is shown in Fig. 1. A high power laser beam is delivered to a sample that

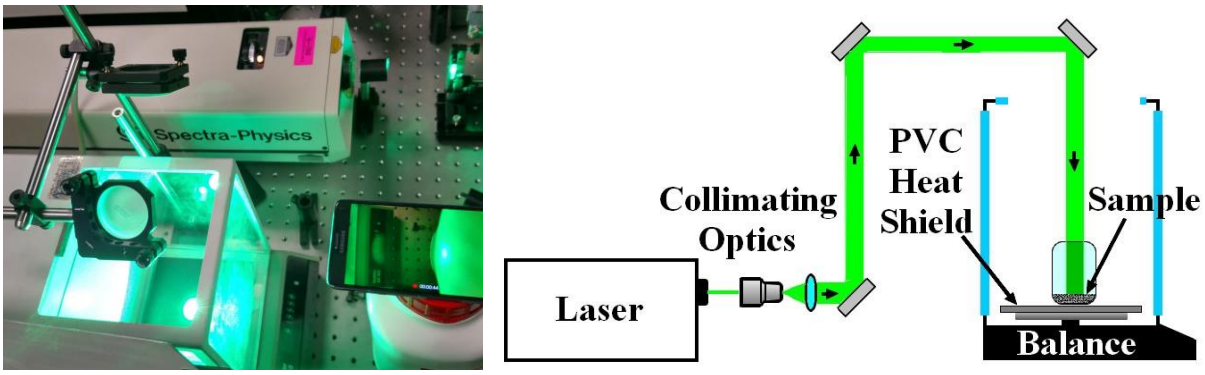


Figure 1. Experimental setup: (left) photo and (right) diagram.

sits atop a scientific balance, and propellant is ablated via thermal decomposition as the mass is observed.

In our experiments, an argon ion laser (Spectra-Physics, SpectraLite^{TM} 2017) was the thermal source. The laser was operated at 514.5 nm wavelength and up to 2.0 W output power, measured using the internal power sensor in the laser head and independently verified up to 0.6 W using a thermal power sensor (Thorlabs, S401C). During the experiments, the laser was switched on using the manual shutter switch at the aperture. The wavelength dial setting used was 515 nm, the internal iris was set to the largest setting ("10"), and the beam power was optimized to 2.0 W before the experiments. The argon laser had a nominal beam diameter of 1.4 mm and a nominal beam divergence of 0.5 mrad, with beam parameter product $M^2 \approx 1$. The laser beam spot area was measured at 2.9 ± 0.2 mm^2 at the laser aperture using thermally sensitive paper. The beam was directed through a collimating telescope (-300 mm focal length diverging lens and +25 mm doublet lens with 30 mm focal length) to form a roughly circular laser beam spot of 17 ± 3 mm^2, then directed by way of three aluminized mirrors, passing through the top glass shield of our scientific balance, and finally arriving at the target with area 4.8 ± 0.8 mm^2, achieving an estimated irradiance at target of 41 ± 7 W/cm^2.

Samples were chemically prepared using standard, laboratory-grade reagents from the Saint Cloud State University Department of Chemistry. These reagents included ammonium carbonate, sodium bicarbonate, magnesium carbonate, and graphite powder. The individual carbonates were ground to a fine powder using a mortar and pestle for 60 seconds, then subsequently added to a specified mass of graphite powder. Once thoroughly shaken, the sample mixture was packed tightly into a glass dish. In each experiment, the sample was irradiated for 60 seconds. This procedure was repeated 10 times for each sample, always beginning on a fresh surface.

Mass measurements needed to be conducted in real time in order to accurately and precisely estimate the chemical decomposition rate. A digital scientific balance (Mettler AE163) with nominal ±10 μg readability and about ±30 μg precision was used to measure mass. The scale was leveled and zeroed before each experimental run. The output reading of the scale was monitored throughout each 60 second experiment.

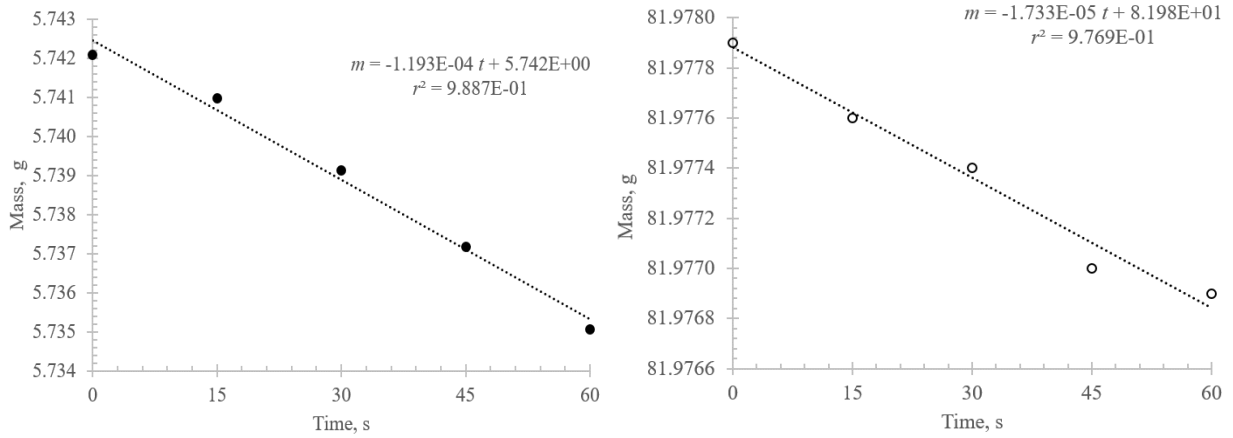
Before beginning tests with the laser, samples of the graphite, ammonium carbonate, and sodium bicarbonate were set in the test environment and monitored with data recorded at intervals of 15 seconds. These calibration data establish the baseline behavior of the samples in the room temperature environment of our laboratory. The baseline systematic errors for mass rates were 2.7 ± 1.3 μg/s for pure ammonium carbonate, 0.33 ± 0.08 μg/s for pure sodium bicarbonate measured over 900 s, and 0.05 ± 1.21 μg/s for graphite. We now turn to a presentation of the experimental results.

III. Results and Discussion

Initially, we set out to study sodium bicarbonate, ammonium carbonate, and magnesium carbonate as propellant candidates. However, initial tests on a magnesium carbonate sample did not produce significant mass loss, and this compound was removed from consideration. Tests proceeded with ammonium carbonate and sodium bicarbonate.

A. Ablation Rate Results

Two examples of mass removal test results for ammonium carbonate and sodium bicarbonate are shown in Fig. 2

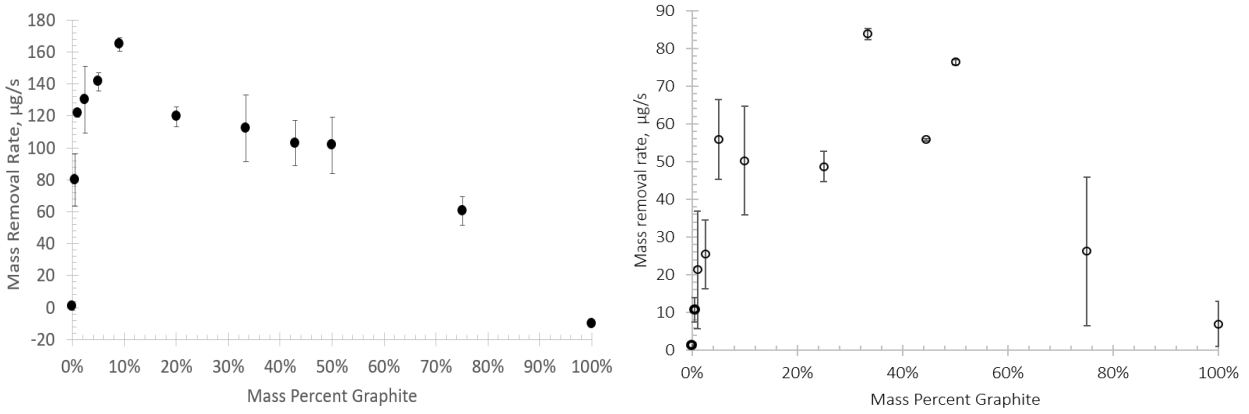


(a) **(b)**

Figure 2. Typical raw mass removal data and fitted mass removal rate for 1% carbon doped propellant mixes for (a) ammonium carbonate and (b) sodium bicarbonate.

for context. The decomposition mass loss rate was highly linear throughout the 60 second period. Mass removal rate was calculated for each experiment using a linear best fit of the slope of the recorded masses over the time period of

irradiation. Mass measurements were made every 15 seconds within the 60 second period (i.e., at 0, 15, 30, 45, and 60 s). Ten trials were conducted for each data point to enable error analysis. Tests were performed across the entire range of propellant mixtures from 0–100% carbon doping, for both ammonium carbonate and sodium bicarbonate. Error values were calculated as one standard deviation. The data are presented in Fig. 3.



(a) **(b)**

Figure 3. Mass removal rate under laser irradiation in air as a function of graphite doping for (a) ammonium carbonate and (b) sodium bicarbonate.

In the ammonium carbonate data, one can observe a rapid rise in mass loss as carbon doping increases to 1%, which we attribute to a transition from reflecting to absorbing behavior. Below this limit, not much of the incoming laser radiation is absorbed, so little vaporization occurs. Above the limit, sufficient carbon is present to absorb and transfer power to the propellant powder grains and achieve mass removal. However, as the fraction of carbon f increases, there is less propellant to vaporize, since the carbon itself is essentially inert ($T_s \approx 4000$ K, but an oxidation reaction can be accessed in air below 1000 K). Thus, at higher percentages of carbon doping, the mass loss falls off approximately linearly, with a functional form proportional to $1 - f$.

The experimental results for sodium bicarbonate are less transparently interpreted. The initial rise in mass loss rate with increasing carbon content is not as sharp, and the mass loss rate does not fall off as quickly as it does for ammonium carbonate. The reasons for these differences are as yet unclear.

The experiments in this study demonstrate mass loss from certain carbonates due to chemical decomposition at relatively low temperatures. We are interested in further exploring these materials as laser propulsion propellants.

IV. Conclusions

This study explored the development of carbon-doped carbonates as chemical propellants for laser propulsion. Ammonium carbonate, sodium bicarbonate, and magnesium carbonate were tested due to their low decomposition temperatures and relatively low toxicity. The samples were irradiated by a 2.0 W argon laser beam at 514.5 nm wavelength and 41 ± 7 W/cm^2 irradiance, and mass removal was measured using a digitial scientific balance. No significant mass loss was measured for magnesium carbonate, but significant mass losses were noted for both ammonium carbonate and sodium bicarbonate. The mass loss rate increased sharply upon addition of up to a few percent carbon (graphite) to the propellant material. With increasing percentages of carbon above a maximum, the mass loss rate decreased at an approximately linear rate to zero mass removal for 100% graphite. The peak mass removal rates were approximately 164.8 ± 4.1 μg/s for ammonium carbonate, and 83.8 ± 1.5 μg/s for sodium bicarbonate. For the future, we plan to explore the dependence of mass loss rate upon the irradiance of the laser beam, and incorporate the materials into laser propulsion experiments as propellants.

Acknowledgments

This work was funded by a 2015 St. Cloud State University (SCSU) University Researcher Award, a 2016 SCSU New Researcher Award, and a 2016 SCSU Student Research Award. Generous support was provided by the Saint Cloud State University Department of Physics & Astronomy, the Department of Chemistry and Biochemistry, and generally by the College of Science & Engineering of St. Cloud State University. Support was also provided by the Institute for Materials, Energetics and Complexity and particularly from Dr. C. Adam Schlecht. Students David Corgard and Sam Hartman assisted with this research project.

References

[1]Marx, G., "Interstellar Vehicle Propelled by Terrestrial Laser Beam," *Nature*, Vol. 211, 2 July 1966, pp. 22-23.

[2]Kantrowitz, A., "Propulsion to Orbit by Ground-Based Lasers," *Astronautics & Aeronautics*, Vol. 10, No. 5, 1972, pp. 74-76.

[3]Pakhomov, A. V., Thompson, M. S., Swift, W. Jr., and Gregory, D. A., "Ablative Laser Propulsion: Specific Impulse and Thrust Derived from Force Measurements," *AIAA Journal*, Vol. 40, No. 11, 2002, pp. 2305-2311.

[4]Urech, L., Lippert, T., Phipps, C. R., and Wokaun, A., "Polymers as fuel for laser-based microthrusters: An investigation of thrust, material, plasma and shockwave properties," *Applied Surface Science*, Vol. 253, No. 19, 2007, pp. 7646-7650.

[5]Sinko, J. E. and Pakhomov, A. V., "Laser Propulsion with Liquid Propellants Part I: an Overview," *Proceedings of the Fifth International Symposium on Beamed Energy Propulsion*, ed. A. V. Pakhomov, AIP Conference Proceedings, Vol 997, American Institute of Physics, Melville, NY, 2008, pp. 195-208.

[6]Pakhomov, A. V., and Sinko, J. E., "A Conceptual Tree of Laser Propulsion" in *Proceedings of the Fifth International Symposium on Beamed Energy Propulsion*, ed. A. V. Pakhomov, AIP Conference Proceedings, Vol. 997, American Institute of Physics, Melville, NY, 2008, pp. 592-603.

[7]Dyer, P. E., Pervolaraki, M., and Lippert, T., "Experimental studies and thermal modelling of 1064- and 532-nm Nd:YVO_4 micro-laser ablation of polyimide," *Applied Physics A*, Vol. 80, No. 3, 2005, pp. 529-536.

[8]Bityurin, N., Luk'yanchuk, B. S., Hong, M. H., and Chong, T. C., "Models for Laser Ablation of Polymers," *Chemical Reviews*, Vol. 103, No. 2, 2003, pp. 519-552.

[9]Marla, D., Bhandarkar, U. V., and Joshi, S. S., "A model of laser ablation with temperature-dependent material properties, vaporization, phase explosion and plasma shielding," *Applied Physics A*, Vol. 116, No. 1, 2014, pp. 273-285.

[10]Sinko, J. E., "Laser Ablation Propulsion Tractor Beam System," *Journal of Propulsion and Power*, Vol. 26, No. 1, Jan.-Feb. 2010, pp. 189-191.

[11]Sinko, J. E. and Schlecht, C. A., "CO_2 Laser Ablation Propulsion Tractor Beams," *Proceedings of the 6th International Symposium on Beamed Energy Propulsion*, AIP Conference Proceedings, Vol. 1230, eds. C. Phipps, K. Komurasaki, and J. Sinko, American Institute of Physics, Melville, NY, 2010, pp. 282-294.

[12]Sinko, J., Schlecht, C., Lis, T., Davidson, R., Gregory, D., Yokota, S., Harada, S., Sasoh, A., Oh, B., and Larus, M., "Laser Ablation Tractor Beaming with Bilayer Targets," *50th AIAA Aerospace Sciences Meeting*, AIAA, Washington, DC, 2012.

[13]Weast, R. C., Astle, M. J., and Beyer, W. H., eds., *CRC Handbook of Chemistry and Physics*, 69th Ed., CRC Press, Boca Raton, FL, 1988-1989, "Physical Constants of Inorganic Compounds," pp. B-68–B-146.

[14]L'vov, B. V., "Mechanism of thermal decomposition of alkaline-earth carbonates," *Thermochimica Acta*, Vol. 303, No. 2, 1997, pp. 161-170.