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CHARACTERIZING HIGH-ENERGY-DENSITY PROPELLANTS FOR SPACE PROPULSION APPLICATIONS

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ABSTRACT

A technique for determining the thermophysical properties of high-energy-density matter (HEDM) propellants is presented. HEDM compounds are of interest in the liquid rocket engine industry due to their high density and high energy content relative to existing industry standard propellants (liquid hydrogen, kerosene, and hydrazine). In order to model rocket engine performance, cost, and weight in a conceptual design environment, several thermodynamic and physical properties are needed. These properties include enthalpy, entropy, density, viscosity, and thermal conductivity. These properties need to be known over a wide range of temperature and pressure. A technique using a combination of quantum mechanics and molecular dynamics is used to determine these properties for quadricyclane, a HEDM compound of interest. Good agreement is shown with experimentally measured thermophysical properties. A vehicle case study is provided to quantify the system level benefits of using quadricyclane instead of hydrazine for the lunar lander ascent stage of the Exploration Systems Architecture Study. The results show that the use of HEDM propellants can significantly reduce the lunar lander mass and indicate that HEDM propellants are an attractive technology to pursue for future lunar missions.

NOMENCLATURE

CCD	=	central composite design
COMPASS	=	Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies
DMAZ	=	2-azido-N,N dimethylethanamine ($C_4H_{10}N_4$)
DOE	=	design of experiments
Engine T/W	=	engine thrust / engine weight
ESAS	=	Exploration Systems Architecture Study
GAMESS	=	General Atomic and Molecular Electronic Structure System
HEDM	=	high-energy-density matter
HF	=	Hartree-Fock

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LAMMPS	=	Large-scale Atomic/Molecular Massively Parallel Simulator
LH2	=	liquid hydrogen
LOX	=	liquid oxygen
I_{sp}	=	specific impulse (seconds)
MMH	=	monomethyl hydrazine
N_2O_4	=	nitrogen tetraoxide
NPSS	=	Numerical Propulsion System Simulation
O/F	=	oxidizer-to-fuel ratio
POST	=	Program to Optimize Simulated Trajectories
REDTOP-2	=	Rocket Engine Design Tool for Optimal Performance Release 2
RMS	=	root mean square
ROCETS	=	Rocket Engine Transient Simulation
RP-1	=	refined petroleum 1 (kerosene)
SSDL	=	Space Systems Design Lab
UDMH	=	unsymmetrical dimethyl hydrazine
WBS	=	weight breakdown structure
ε	=	nozzle expasion ratio (exit area / throat area)

INTRODUCTION

There exists wide ranging research interest in high-energy-density matter (HEDM) propellants as a potential replacement for existing industry standard fuels (LH2, RP-1, MMH, UDMH) for liquid rocket engines. The U.S. Air Force Research Laboratory [1,2], the U.S. Army Research Lab [3,4], the NASA Marshall Space Flight Center [5], and the NASA Glenn Research Center [6,7] each either recently concluded or currently has ongoing programs in the synthesis and development of these potential new propellants.

Most conceptual rocket engine powerhead design tools (e.g. NPSS, ROCETS, and REDTOP-2) require several thermophysical properties of a given propellant in order to perform conceptual vehicle designs. These properties include enthalpy, entropy, density, viscosity, and thermal conductivity. For most of these potential new HEDM propellants, this thermophysical data either does not exist or is incomplete over the range of temperature and pressure necessary for liquid rocket engine design and analysis.

If one wishes to use HEDM propellants in a conceptual vehicle design, a technique for determining the thermophysical properties of these propellants must be used. Current computational techniques cannot model complex HEDM molecules to the level of accuracy needed for rocket engine powerhead design tools. As a result, a technique for determining the thermophysical properties of potential new rocket engine propellants has been developed and is presented. This technique uses a combination of analytical/computational methods and experimental investigations. Quantum mechanics and molecular dynamics are used to model these new HEDM propellants at a molecular level. By modeling the motion and distribution of the simulated molecules, one can calculate all the thermophysical properties of interest. Experimental investigations are performed to both verify and improve the predictive accuracy of the computational methods.

Results are provided for quadricyclane, a HEDM fuel of interest. A ball and cylinder model of quadricyclane is shown in Figure 1. Quadricyclane is a hydrocarbon compound that is a liquid at standard temperature and pressure.

The calculated thermophysical properties are compared against experimental measurements and good agreement is achieved. The results of a conceptual vehicle

design case study utilizing the calculated thermophysical properties of quadricyclane are presented. The case study chosen is the lunar lander ascent stage of NASA's proposed lunar Exploration Systems Architecture Study (ESAS). This case study helps to quantify the weight and performance benefits of using quadricyclane over existing industry standard hydrocarbon fuels for space propulsion applications.
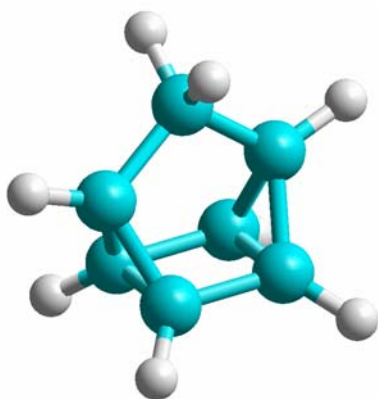

Figure 1: Ball and cylinder rendering of quadricyclane (C_7H_8)

ANALYSIS TECHNIQUE

The method used to calculate the necessary thermophysical properties for HEDM propellants is broken down into three main parts. The first part is the use of quantum mechanics energy calculations to determine the intramolecular energy surface of the compound of interest. The second part is the use of molecular dynamics to determine the density, enthalpy change, and entropy change of the compound of interest at a range of temperatures and pressures. The third part is the use of additivity methods to determine the kinematic viscosity and thermal conductivity of the compound of interest at the same temperature and pressure ranges from part two. Together these three parts enable the determination of all the necessary thermophysical properties of rocket fuels for conceptual rocket engine powerhead design.

Quantum Mechanics

Quantum mechanics is used to determine the potential energy surface of the compound of interest. This analysis of the potential energy surface is used to create a curve-fit which is input into molecular dynamics codes to model

the potential energy between atoms and molecules in a simulation.

The COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field model is one such potential energy model. As the name implies, the COMPASS model is a molecular force field model which is optimized for condensed-phases [8,9,10,11]. This model is particularly useful for predicting thermophysical properties for rocket propellants because the propellant is in a condensed phase for the majority of the time it is running through the different engine components.

In order to determine the coefficient values for the valence terms of the COMPASS model (first ten terms of Figure 2) for a particular molecule, quantum mechanical analysis of the molecule is needed. This analysis is done using an industry standard quantum chemistry program package developed at Iowa State University called the General Atomic and Molecular Electronic Structure System (GAMESS) [12].

$$
\begin{aligned}
E^{COMPASS} =& \sum_b \left[k_2(b-b_0)^2 + k_3(b-b_0)^3 + k_4(b-b_0)^4 \right] \\
&+ \sum_\theta \left[h_2(\theta-\theta_0)^2 + h_3(\theta-\theta_0)^3 + h_4(\theta-\theta_0)^4 \right] \\
&+ \sum_\phi \left[V_1(1-cos\,\phi) + V_2(1-cos\,2\phi) + V_3(1-cos\,3\phi) \right] \\
&+ \sum_\chi K_\chi(\chi-\chi_0)^2 \\
&+ \sum_{b,b'} K_{bb'}(b-b_0)(b'-b_0') \\
&+ \sum_{\theta,\theta'} K_{\theta\theta'}(\theta-\theta_0)(\theta'-\theta_0') \\
&+ \sum_{b,\theta} K_{b\theta}(b-b_0)(\theta-\theta_0) \\
&+ \sum_{b,\phi} (b-b_0)\left[G_1\,cos\,\phi + G_2\,cos\,2\phi + G_3\,cos\,3\phi \right] \\
&+ \sum_{\theta,\phi} (\theta-\theta_0)\left[F_1\,cos\,\phi + F_2\,cos\,2\phi + F_3\,cos\,3\phi \right] \\
&+ \sum_{\theta,\theta',\phi} K_{\theta\theta'\phi}(\theta-\theta_0)(\theta'-\theta_0')cos\,\phi \\
&+ \sum_{i,j} \frac{q_i q_j}{r_{ij}} \\
&+ \sum_{i,j} \varepsilon_{ij}\left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^9 - 3\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 \right]
\end{aligned}
$$

Figure 2: COMPASS Force-Field Potential Function

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The process used to determine these coefficients is one developed by Maple et al [13]. A brief description of this process is provided here. For a more extensive description, please see Maple's paper.

The potential energy surface is probed at several different points (molecular configurations) using GAMESS. The energy and first and second Cartesian derivatives are calculated for each molecular configuration. A gradient-based optimizer is used to fit the COMPASS model parameters (k_2, k_3, k_4, h_2, h_3, h_4, V_1, V_2, V_3, K_χ, $K_{b\theta}$, $K_{\theta\theta'}$, $K_{b\theta}$, G_1, G_2, G_3, F_1, F_2, F_3, and $K_{\theta\theta'\phi}$ in Figure 2) with the objective being the best approximation of the quantum mechanically predicted potential energy surface.

These parameters affect the dynamics of the bond, angle, torsional, and out-of-plane motion (Figure 3) of the atoms within the molecule.
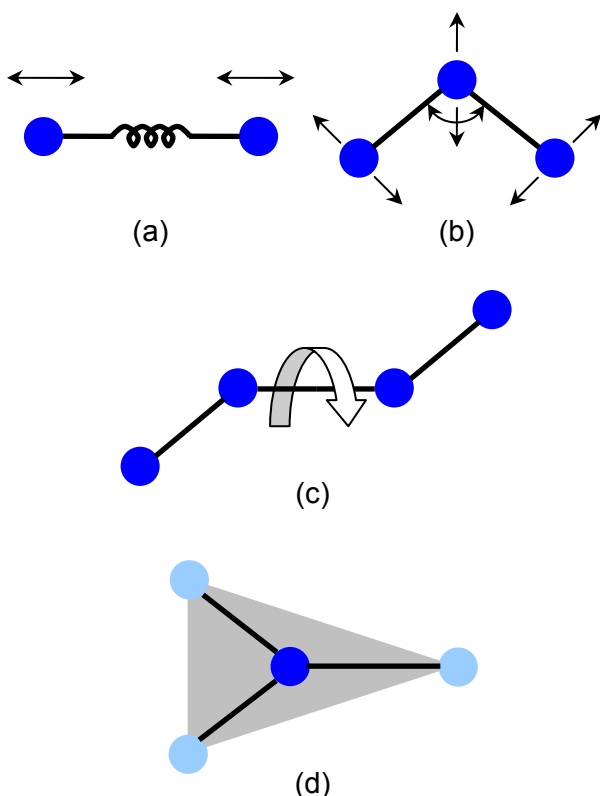

Figure 3: (a) Bond, (b) Angle, (c) Torsion, and (d) Out-of-Plane Internal Motions

The energy calculation method chosen in GAMESS is the Hartree-Fock method with the 6-31G* basis set [14]. The Hartree-Fock method is an approach for solving the Schrödinger wave equation numerically. The Schrödinger wave equation describes the location of all the particles in the system as a function of time. A basis set is a set of functions used in quantum chemistry calculations to represent the atomic and molecular orbitals [15:545-546]. The 6-31G* basis set has been shown to be effective for use in the creation of molecular dynamics force fields [16].

Molecular Dynamics

Once an accurate approximation of the quantum mechanical energy surface has been created, that approximation (Figure 2) can then be used in molecular dynamics simulations. Molecular dynamics is a technique for modeling the positions and velocities of particles subject to the laws of classical mechanics [17]. A molecular dynamics example of liquid 2-azido-N, N-dimethyl-ethanamine (DMAZ) is provided in Figure 4.
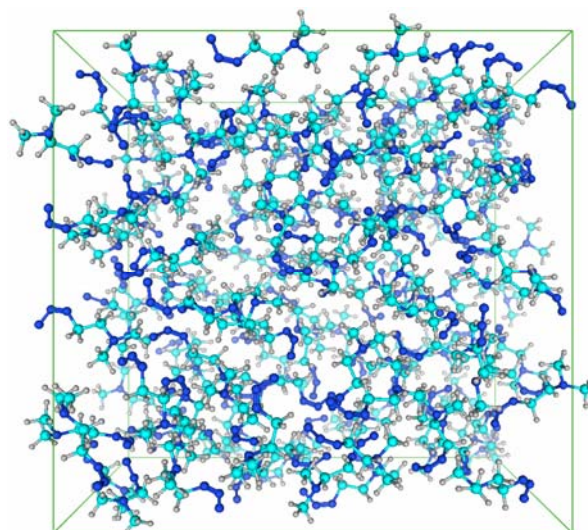

Figure 4: Liquid DMAZ ($C_4H_{10}N_4$) Molecular Dynamics Example

Force is applied to each particle as a result of the potential energy between that particle and other particles in the system. As the molecular dynamics model is propagated through time, one can compute the internal energy and density of the system. The internal energy can then be used to calculate the enthalpy and entropy of the system.

Molecular dynamics simulations are typically run at a constant number of particles, constant temperature, and either constant volume or constant pressure. The first

simulation type is known as a NVT simulation (N=number of molecules, V=volume, T=temperature) while the second is known as a NPT simulation (P=pressure). For the work performed here, an initial molecular configuration is input (typically a grid of quadricyclane molecules lined up along the three Cartesian axes). A NVT simulation is then run at the desired temperature using a very small time step (~0.1 fs) to relieve any stresses that may have been inadvertently introduced into the system with the initial configuration. After this initial NVT phase, a NPT phase is then used to gather energy and density data at the desired temperature and pressure.

The molecular dynamics simulations were performed using Sandia National Laboratories' Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [18]. Simulations of 125 molecules were performed using periodic boundary conditions [19]. Long-range corrections were used on both the van der Waals (sharp cutoff at 7.5 angstroms, with an energy and pressure tail correction) and electrostatic potentials (particle-particle particle-mesh) [18]. The NVT phase consisted of a 200,000 time step, 0.1 fs/step run. The NPT phase consisted of a 1-2 million time step, 0.5 fs/step run. Data was recorded after approximately 500,000 time steps into the NPT phase. By that point in the NPT phase, temperature, pressure, energy, and density have converged.

For this work, the molecular dynamics simulations are used for two purposes. The first purpose is to determine the best values for the intermolecular parameters of the COMPASS force-field model (last two terms of Figure 2). Once this is done, the second purpose is to determine the enthalpy, entropy, and density of the molecule of interest over the entire range of temperature and pressure experienced in a liquid rocket engine.

<u>Intermolecular Parameter Values</u>

In order to determine the best values for the intermolecular parameters, molecular dynamics simulation results are compared with experimental enthalpy, entropy, and density data. Due to the fact that there is limited experimental data for HEDM compounds, model compounds are used for

intermolecular parameter determination. A model compound is chosen for each HEDM compound. Model compounds are chosen based upon their similarity to the corresponding HEDM compound (bond structure and atom types) and the availability of extensive experimental data. For quadricyclane, the model compound norbornane is used. A ball and cylinder model of norbornane is provided in Figure 5. Norbornane is chosen because it has a bicyclic ring structure similar to that of quadricyclane.
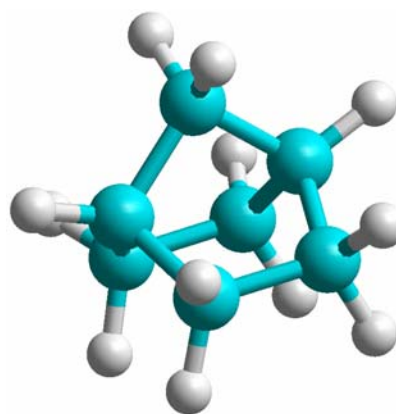

Figure 5: Ball and cylinder rendering of norbornane (C_7H_{12})

The intermolecular parameters (σ and ε for the different types of atoms) are then adjusted to improve the accuracy of the molecular dynamics simulations at predicting density. A design of experiments (DOE) is performed on the intermolecular parameters to determine the sensitivity of density to changes in these parameters. A central composite design (CCD) is the DOE chosen for this work. For norbornane, there are six intermolecular parameters that are adjusted: ε and σ for each atom type. There are three atom types: a carbon atom attached to two or fewer heavy atoms (denoted c4), a carbon atom attached to three or more heavy atoms (denoted c43), and a hydrogen atom (denoted h1). With six design variables, the CCD requires 47 runs (including three center points). That is, 47 molecular dynamics runs are required to sufficiently model the sensitivity of density to the six intermolecular parameters.

A response surface is created to relate the predicted density from the molecular dynamic

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simulations to the settings for the intermolecular parameters. This response surface, which is simply a multidimensional curve-fit, is fit to the molecular dynamics DOE runs. The response surface equation chosen includes the first order and second order main effects plus all second order cross terms. For six design variables, this results in 28 coefficients that must be fit to create the response surface.

Once the response surface is created, an optimizer is used to minimize the difference between the predicted density out of the molecular dynamics simulation with the corresponding experimental value. Validation molecular dynamics runs are then performed using the optimized parameters to verify that the predicted thermophysical values from the response surface match the molecular dynamics results.

Thermophysical Property Determination

With the corrected intramolecular parameters (from the quantum mechanics step) and the corrected intermolecular parameters (from the first part of the molecular dynamics step), one can now compute the thermophysical properties of the HEDM compound of interest. The range of temperature and pressure, which is determined by the anticipated operating range of the rocket engine, is used to map out the required molecular dynamics runs. For quadricyclane, the temperature ranges from 280–400K while the pressure ranges from 14.7–1500 psi. Runs are performed at the following temperatures (K): 280, 300, 350, and 400. Runs are performed at the following pressures (psi): 14.7, 500, 1000, and 1500. This results in 4 temperatures and 4 pressures, or 16 molecular dynamics runs.

Enthalpy is determined with the following equations:

$$h(T,P) = \Delta h_f^0 + h_{MD}(T,P) - h_{MD}(T_0,P_0)$$

$$h_{MD}(T,P) = E_{kin}(T,P) + E_{pot}(T,P) + \frac{P}{\rho}$$

$$E_{kin} = \frac{1}{2N} \sum_{i=1}^{N} m_i (\vec{v}_i \cdot \vec{v}_i)$$

$$E_{pot} = E^{COMPASS} \; (\text{ from Figure 2 })$$

The left hand side of the first equation is the desired total enthalpy. The first term on the right hand side of the first equation is the enthalpy of formation.

The enthalpy of formation, Δh_f^0, is typically defined as the enthalpy of the particle at 298K and 1 atm. with respect to the arbitrary base in which the enthalpy of the elements that make up that particle is chosen to be zero in their natural states at the same temperature and pressure [20]. The enthalpy of formation is taken either from literature or from quantum mechanics results.

The second term on the right hand side of the first equation is the enthalpy calculated by molecular dynamics at the desired temperature and pressure. The third term on the right hand side of the first equation is the enthalpy calculated by molecular dynamics at 298K and 1 atm. The E_{kin} term is the kinetic energy of the particles. In the E_{kin} equation, N is the number of particles in the system and m_i and $\vec{v}_i$ are the respective mass and velocity of particle i. The E_{pot} term is the potential energy calculated from the COMPASS energy potential.

Temperature, pressure, and density are determined with the following equations:

$$T = \frac{2E_{kin}}{3k_B}$$

$$P = \frac{Nk_BT}{V} + \frac{1}{3V} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \sum_{\alpha=1}^{n} \sum_{\beta=1}^{n} \vec{f}_{ij}^{\alpha\beta} \cdot \vec{r}_{ij}^{\alpha\beta}$$

$$\rho = \frac{N}{V} \sum_{i=1}^{N} m_i$$

In the first equation above, k_B is Boltzmann's constant. V is the volume of the computational space, $\vec{f}_{ij}^{\alpha\beta}$ is the force vector of atom β of molecule j on atom α of molecule i, and $\vec{r}_{ij}^{\alpha\beta}$ is the position vector from atom β of molecule j to atom α of molecule i. The first term on the right hand side of the pressure equation is the ideal gas term while the second term is the configurational or "virial" term which becomes prominent at higher densities (farther away from the ideal gas assumption).

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Finally, entropy is defined from enthalpy with the equations below. Like Δh_f^0, Δs_f^0 is typically taken from quantum mechanics results.

$$s(T,P) = \Delta s_f^0 + s_{MD}(T,P)$$

$$s_{MD}(T,P) = \int_{298K}^{T} \frac{C_p(\tau,P)}{\tau} d\tau$$

$$C_p(T,P) = \frac{h_{MD}(T_2,P_2) - h_{MD}(T_1,P_1)}{T_2 - T_1}$$

Additivity Methods

Additivity methods are used to compute the kinematic viscosity and thermal conductivity of the propellants of interest. Additivity methods are used, instead of molecular dynamics, because kinematic viscosity and thermal conductivity have less of an affect on the engine parameters of interest (specific impulse, engine weight) than do density, enthalpy, and entropy. As a result, a less accurate, but easier and computationally less expensive method can be used.

Additivity methods make use of the observation that a substance's physical properties depend on that substance's particular molecular structure [21,22:24]. Benson and Buss [23] in 1958 showed that it was possible to make a system of "additivity rules" to determine certain thermodynamic and physical properties of substances based upon their atom, bond, and group makeup. Individual contributions from atoms, bonds, and groups to the estimated values of thermophysical properties can be calculated by regressing empirical thermophysical data for known substances.

For this work, the additivity parameter method developed by Chung et al. is used for its ability to handle many different molecules over a wide range of temperature and pressure [24]. This method is implemented in an Excel spreadsheet and therefore calculations can be performed very rapidly. Kinematic viscosity and thermal conductivity calculations are performed over the same temperature and pressure ranges used for the molecular dynamics simulations for quadricyclane (280 K ≤ T ≤ 400 K; 14.7 psi ≤ P ≤ 1500 psi).

RESULTS

The computational results show that this method is capable of predicting the thermophysical properties of rocket engine propellants with sufficient accuracy for conceptual vehicle design.

Thermophysical Property Calculations

The molecular dynamics results for the enthalpy, entropy, and density of quadricyclane match experimental data well over the range of temperature and pressure modeled. All experimental data is taken from reference 1.

The root mean square (RMS) errors are: 5.89% for sensible enthalpy, 3.65% for sensible entropy, and 0.36% for density. These errors are all well within the limits required for conceptual engine powerhead design. A multiplication factor of 0.39 is used for internal energy calculations for all LAMMPS runs. The source of this factor is currently being investigated.
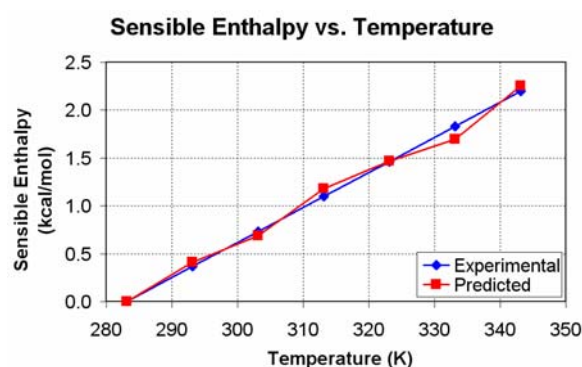

Figure 6: Quadricyclane Sensible Enthalpy vs. Temperature
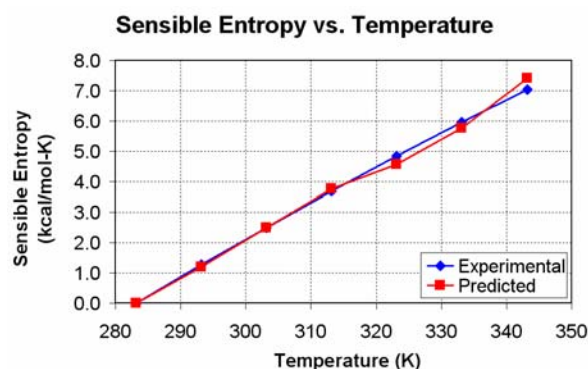

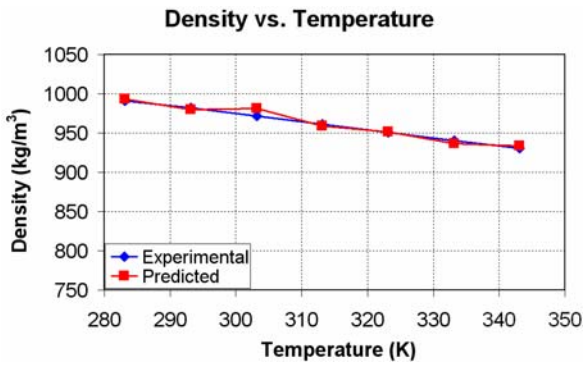Figure 7: Quadricyclane Sensible Entropy vs. Temperature

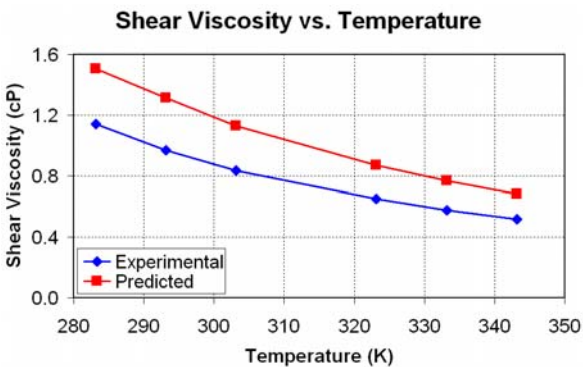Figure 8: Quadricyclane Density vs. Temperature

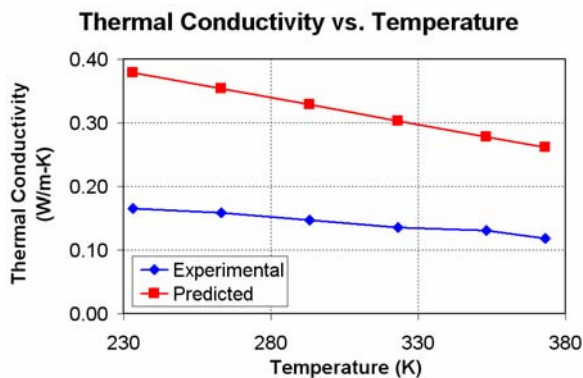Figure 9: Quadricyclane Shear Viscosity vs. Temperature

Figure 10: Quadricyclane Thermal Conductivity vs. Temperature

The results for viscosity (Figure 9) and thermal conductivity (Figure 10) show the same trends as the experimental results and are within accuracy requirements for conceptual engine analysis. The errors found using additivity methods for the prediction of viscosity and thermal conductivity are larger than the molecular dynamics results for enthalpy, entropy, and density. A sensitivity study was performed to capture how sensitive I_{sp} is to changes in viscosity and thermal conductivity.

This sensitivity study used the NASA rocket engine powerhead design code ROCETS. Multipliers were applied to the different thermophysical properties used in ROCETS. The results of the sensitivity study show that an order of magnitude change in viscosity changes I_{sp} by only 0.01%. An order of magnitude change in thermal conductivity changes I_{sp} by only 0.02%. These sensitivity results indicate that the additivity method predictions of these properties are well within the accuracy requirements for conceptual rocket engine design.

Case Study

Using the thermophysical property calculations for quadricyclane, a vehicle case study of the lunar lander descent and ascent stages for the NASA ESAS architecture was performed. Figure 11 is a rendering of the Lunar Surface Access Module (LSAM) from the ESAS Final Report [25].
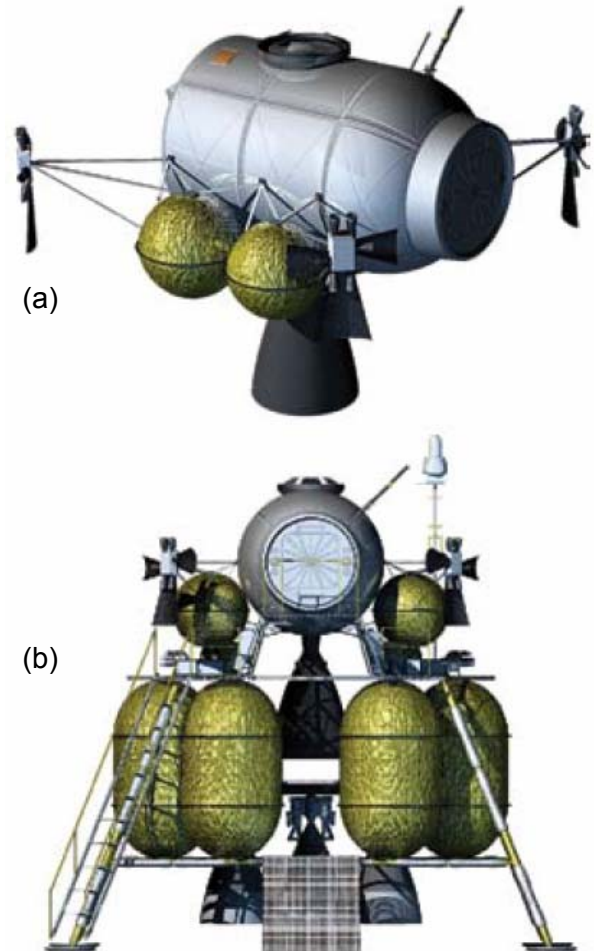

(a)

(b)

Figure 11: ESAS Baseline LSAM [25]:
(a) Ascent stage
(b) Ascent + Descent Stages

Propulsion analysis was performed using REDTOP-2, a commercial rocket engine powerhead design tool. POST 3-D was used for ascent and descent trajectory analysis. POST is an industry standard trajectory optimization and analysis tool.

For this work, two designs were performed: (1) a LSAM which uses hypergolic propellants for the ascent stage engine, and (2) a LSAM which uses quadricyclane and LOX for the ascent stage engine. In both cases, the descent stage propulsion system consists of four LOX/LH2 expander cycle engines derived from the RL-10 engine family [25].

The ESAS Final Report details three different lunar missions. The first is a lunar sortie crew with cargo mission which is a global access mission for four crew members with a surface stay of 7 days. The second is a lunar outpost cargo delivery mission which delivers 20 mT of cargo to the lunar surface. The third is a lunar outpost crew with cargo mission that delivers four crew members plus cargo for a surface stay of 6 months. For this work, the LSAM is designed for the first mission type (cargo plus crew for 7 days). Table 1 provides a listing of the mission parameters and assumptions made for this case study.

Table 1: Mission Parameters

Parameter	Value
Number of Crew	4
Payload to Lunar Surface	2294 kg
Mission Time	7 days
On-orbit Time	150 days
Dry Weight Margin	17%

The LSAM hypergolic propellants are nitrogen tetraoxide (N_2O_4) and monomethyl hydrazine (MMH). Table 2 provides the ascent stage engine comparison between the hypergolic LSAM ascent stage and the HEDM ascent stage.

The hypergolic propellants have a higher bulk density than the HEDM combination due to the high density of N_2O_4 and the higher oxidizer-to-fuel ratio (O/F). The HEDM engine has a higher I_{sp} due to the higher energy content found in the molecular structure of quadricyclane.

Table 2: Ascent Stage Engine Comparison

	Hypergolic Engine	HEDM Engine
Oxidizer	N_2O_4	LOX
Fuel	MMH	Quad
$\rho_{Oxidizer}$ (kg/m^3)	1450	1141
ρ_{Fuel} (kg/m^3)	880	980
O/F	2.50	2.28
ρ_{Bulk} (kg/m^3)	1287	1092
Expansion Ratio (ε)	85	85
$P_{Chamber}$ (psi)	500	500
Engine T/W	35	35
I_{sp} (sec)	332.3	358.2

Both engines are pressure-fed meaning no pumps are used to increase the pressure from the tanks to the injector. This design allows for a much simpler and thus more reliable system. However, heavier tanks are required because the propellant must be kept at a much higher pressure in the tanks than would be required for a pump-fed system.

The descent stage vehicle thrust-to-weight is 1.85 (using Lunar gravity) and the ascent stage vehicle thrust-to-weight is 2.10 (using Lunar gravity). These values are the same as the Apollo Lunar Module thrust-to-weight values.

Table 3 and Table 4 are the descent stage and ascent stage weight breakdown structures (WBS) for the two different propellant combinations.

As can be seen from Table 3, the use of the HEDM propellant combination provides a total LSAM gross mass savings of over 1,650 kg or 3.0%. Although the bulk density of the HEDM propellants is lower than that of the hypergolic propellants, the increase in tank size due to the lower bulk density (which can be seen in the heavier HEDM ascent stage body group) is more than made up for by the increase in I_{sp} (which can be seen in the lower HEDM descent and ascent propellant weights).

Table 3: Descent Stage WBS

	Hypergolic LSAM	HEDM LSAM
Body Group	5,550	5,360
Main Propulsion	690	670
Primary Power	810	810
PMAD	140	140
Avionics	100	100
Margin	1,240	1,200
Dry Mass	**8,530**	**8,280**
Payload to LS	2,650	2,650
Ascent Stage	12,220	11,670
Residuals/reserves	920	890
Landed Mass	**24,320**	**23,490**
Descent Propellant	30,540	29,710
Startup Losses	270	270
Gross Mass	**55,130**	**53,460**

Table 4: Ascent Stage WBS

	Hypergolic LSAM	HEDM LSAM
Body Group	1,970	1,980
Main Propulsion	250	230
RCS Propulsion	230	230
Primary Power	500	500
PMAD	100	100
Avionics	300	300
Crew Compartment	1,800	1,800
Margin	880	870
Dry Mass	**6,020**	**6,010**
Crew + provisions	560	560
Residuals/reserves	160	140
MECO Mass	**6,750**	**6,710**
RCS Propellant	140	130
Ascent Propellant	5,290	4,770
Startup Losses	60	60
Gross Mass	**12,220**	**11,670**

These results indicate that the use of HEDM propellants may be an attractive option for the LSAM ascent stage engine. Further analysis including cost, operations, reliability, and safety should be done to further flush out the relative advantages and disadvantages of this HEDM propellant combination over hypergolic propellants.

REFERENCES

1. Wucherer, E.J. and A. Wilson. "Chemical, Physical and Hazards Properties of Quadricyclane." U.S. Air Force Research Laboratory, Edwards Air Force Base, California. PL-TR-97-3053, March 1998.

2. Tishkoff, J.M. and M.R. Berman. "Air Force Basic Research in Propellants and Combustion." U.S. Air Force Office of Scientific Research, Arlington, Virginia. AIAA Paper 2002-0901, January 2002.

3. McQuaid, M.J. "Computational Characterization of 2-Azidocycloalkanamines – Notional Variations on the Hypergol 2-Azido-N,N-Dimethylethanamine (DMAZ)." U.S. Army Research Lab. JANNAF 30th Propellant Development and Chracterization Subcommittee Meeting, pp. 45-57, March 2002.

4. McQuaid, M.J. "Structure of Secondary 2-Azidoethanamines: A Hypergolic Fuel vs. a Nonhypergolic Fuel." U.S. Army Research Laboratory, Aberdeen Proving Ground, MD. ARL-TR-3176, April 2004.

5. Bai, S.D., Dumbacher, P., and J.W. Cole. "Development of Advanced Hydrocarbon Fuels at Marshall Space Flight Center." NASA/TP – 2002-211729, May 2002.

6. Palaszewski, B. "Solid Hydrogen Experiments for Atomic Propellants: Particle Formation, Imaging, Observations, and Analyses." NASA Glenn Research Center, Cleveland, Ohio. AIAA Paper 2003-4688, July 2003.

7. Palaszewski, B., Jurns, J., Breisacher, K., and K. Kearns. "Metallized Gelled Propellants Combustion Experiments in a Pulse Detonation Engine." NASA Glenn Research Center, Cleveland, Ohio. AIAA 2004-4191, July 2004.

8. Sun, H., "COMPASS: An ab Initio Force-Field Optimized for Condensed-Phase Applications – Overview with Details on Alkane and Benzene Compounds," *Journal of Physical Chemistry B*, 102: 7338-7364, 1998.

9. Sun, H. and D. Rigby, "Polysiloxanes: ab initio force field and structural, conformational and

thermophysical properties," *Spectrochimica Acta Part A*, 53: 1301-1323, 1997.

10. Rigby, D. and H. Sun, "Computer Simulations of Poly(ethylene oxide): Force Field, PVT Diagram and Cyclization Behaviour," *Polymer International*, 44: 311-330, 1997.

11. Sun, H., Fried, J.R., and P. Ren, "The COMPASS force field: parameterization and validation for phosphazenes," *Computational and Theoretical Polymer Science*, 8: 229-246, 1998.

12. Schmidt, M.W., K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, and J.A. Montgomery, "General Atomic and Molecular Electronic Structure System," *Journal of Computational Chemistry*, Vol. 14: 1347-1363, 1993.

13. Maple, J.R., M.-J. Hwang, T.P. Stockfish, U. Dinur, M. Waldman, C.S. Ewig, and A.T. Hagler, "Derivation of Class II Force Fields. I. Methodology and Quantum Force Field for the Alkyl Functional Group and Alkane Molecules," *Journal of Computational Chemistry*, Vol. 15, No. 2: 162-182, 1994.

14. Hehre, W.J., R. Ditchfield, J.A. Pople, "Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules," *Journal of Chemical Physics*, Vol. 56, No. 5: 2257-2261, 1972.

15. Levine, I.N., Quantum Chemistry, Fifth Edition, Prentice Hall. Upper Saddle River, New Jersey, 2000.

16. Sun, H., J. Mumby, J.R. Maple, and A.T. Hagler, "Ab Initio Calculations on Small Molecule Analogues of Polycarbonates," *Journal of Physical Chemistry*, Vol. 99: 5873-5882, 1995.

17. Frenkel, D. and B. Smit, Understanding Molecular Simulation, From Algorithms to Applications, Academic Press. San Diego, California, 1996.

18. Plimpton, S.J., "Fast Parallel Algorithms for Short-Range Molecular Dynamics," *Journal of Computational Physics*, 117: 1-19, 1995.

19. Allen, M.P. and D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press. Oxford, England, 1987.

20. Van Wylen, G., R. Sonntag, and C. Borgnakke, Fundamentals of Classical Thermodynamics, John Wiley & Sons, Inc. New York, New York, 1994.

21. Joback, K.G., "Cranium: Component Software for Physical Property Estimation", Molecular Knowledge Systems, Inc., Bedford, New Hampshire, 1998.

22. Benson, S.W., Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters, Second Edition, John Wiley & Sons, Inc. New York, New York, 1976.

23. Benson, S.W. and J.H. Buss, "Additivity Rules for the Estimation of Molecular Properties, Thermodynamic Properties," *Journal of Chemical Physics*, Vol. 29, Issue 3: 546-572, 1958.

24. Chung, T-H, Ajlan, M., Lee, L.L. and K.E. Starling, "Generalized Multiparameter Correlation for Nonpolar and Polar Fluid Transport Properties," *Industrial & Engineering Chemistry Research*, Vol. 27: 671-679, 1988.

25. "NASA Exploration Systems Architecture Study Final Report," NASA-TM-2005-214062, November 2005.