

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE Technical Papers		3. DATES COVERED (From - To)	
Please see attached				5a. CONTRACT NUMBER F04611-98-C-0010	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 62203F	
				5d. PROJECT NUMBER 1011	
				5e. TASK NUMBER 00NM	
				5f. WORK UNIT NUMBER	
4. TITLE AND SUBTITLE				8. PERFORMING ORGANIZATION REPORT	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR- ED-TP-2000-205	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT 20030312 061					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	A		Leilani Richardson
Unclassified	Unclassified	Unclassified			19b. TELEPHONE NUMBER (include area code) (661) 275-5015

101100NM

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MEMORANDUM FOR PRS (Contractor/In-House Publication)

FROM: PROI (TI) (STINFO)

24 Oct 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-205**
Suri, Suresh; Tinnierllo, M. & Marcischak, J. (ERC), "Synthesis and Screening of Advanced Hydrocarbon Fuels"

2000 USAF High Energy Density Matter (HEDM) Contractors Conference (Statement A)
(Park City, UT, 24-26 Oct 2000) (Deadline: PAST)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
Comments: _____

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Comments: _____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

PHILIP A. KESSEL
Technical Advisor

Date

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Synthesis & Screening of Advanced Hydrocarbon Fuels

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Jacob Marcischak¹**

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Presentation Outline

- **Goal**
 - HEDM program
 - NASA program
 - IHPRPT program (propellant perspective)
- **Criteria for fuel selection**
- **Approach**
- **Results**
- **Accomplishments (FY-2000)**
- **Planned Efforts (FY-2001)**



HEDM Goal

- To Develop fuels with increased Isp over
LOX/RP-1
 - LOX/RP-1 (Calculated Isp) = 300 sec
 - LOX/RP-1 (Delivered Isp) = 263 sec

**Determined at sea level and 1000 psi chamber
pressure**



IHPRPT GOAL (Propellant Contribution)

To Meet IHPRPT Phase II and Phase III Objective

Phase	Time	Improvement Over SOTA* Isp (del)
II	2005	+ 5 Sec
III	2010	+ 11 Sec

*SOTA: LOX/RP-1 Propellant Isp(del) = 263 Sec.
Isp (calc) = 300 Sec.



NASA Goal

- **FY-1999**
 - Deliver three advanced hydrocarbon fuel in 8-10 lb quantity.
 - Quadricyclane
 - 1,7-Octadiyne
 - Bicyclopentylidene
- **FY-2000**
 - Screen four hydrocarbons for their physical and hazardous properties.



Criteria for Fuel Selection

- Predicts better performance (Isp) over LOX/RP-1 system
- Most desirable physical properties
 - Lower vapor pressure compared to RP-1
 - Higher density ($\geq$ RP-1 = 0.801 g/ml)
 - Freezing point (≤ -10 °C; RP-1 = -41.4 °C)
 - Boiling point $\geq$ B. P. Of RP-1
- Storable
- Compatible with the current system



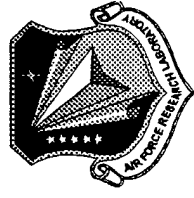
Approach

- Structural requirements
- Survey of energetic hydrocarbons
- Selection of hydrocarbons based on improved theoretical performance
- Synthesis of target hydrocarbons at bench scale.
 - *Easy preparation, cost effective and safe*
- Translate bench-scale synthesis to pilot scale.



Heat of Formation of Saturated Hydrocarbons

Compound	Structure	ΔH_f (Obs)
Ethane	CH_3CH_3	-20.04
Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$	-25.02
Butane	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	-30.03
Pentane	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	-35.08
	$\Delta H_f/\text{added CH}_2 = \sim -5 \text{ Kcal/mole}$	



Heat of Formation of Unsaturated Hydrocarbons

Compound	Structure	$\Delta H_f(\text{Obs})$
Ethylene	$\text{CH}_2=\text{CH}_2$	+12.5
1,3-Butadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	+26.11
	$\Delta H_f/\text{C} = \sim +6.25 \text{ Kcal/mole}$	
Acetylene	$\text{HC}\equiv\text{CH}$	+54.36
	$\Delta H_f/\text{C} = \sim +27.1 \text{ Kcal/mole}$	



Structural Requirement for High Energy Contents (Cont..)

- The energy content is also increased by incorporating strain in the molecule

	ΔH_f
– Ring compound	
– Cyclopropane	+ 12.73 kcal/mole
– Cyclobutane	+ 6.78 kcal/mole
– Cyclopentane	- 18.44 kcal/mole



Structural Requirements For High Energy Contents (Summary)

**Incorporation of small ring (strain) and
unsaturation in a molecule increases its
energy contents**



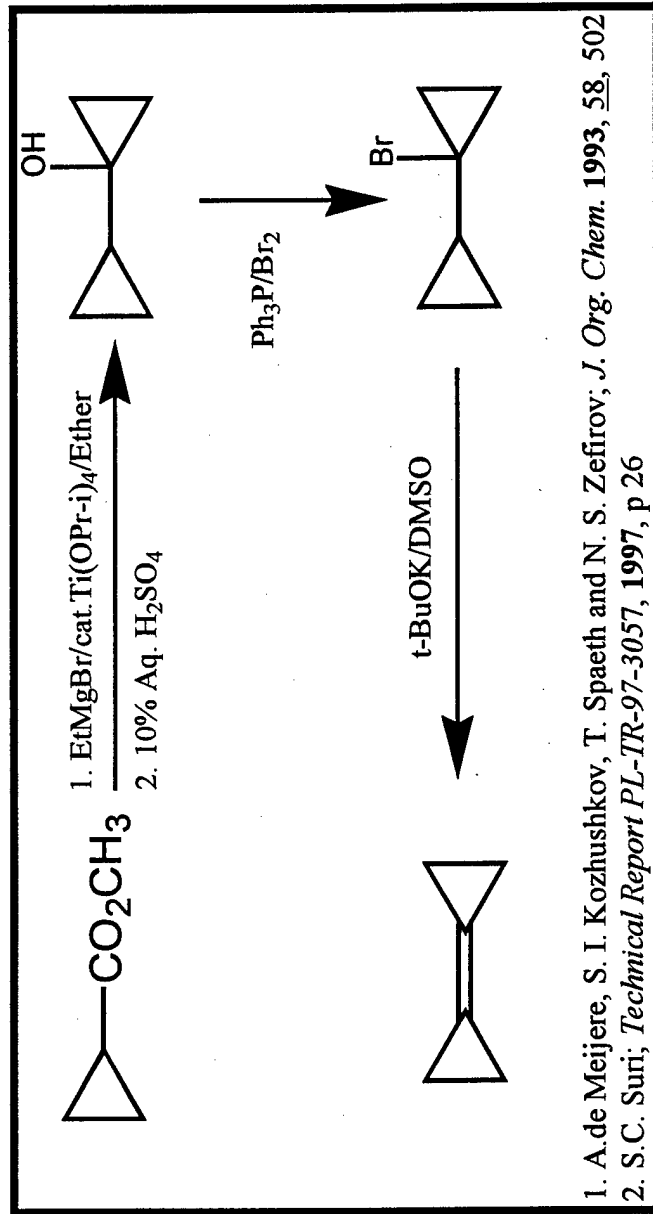
Performance Comparison of Energetic Hydrocarbons (Theoretical)

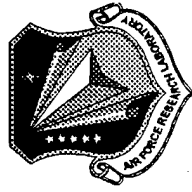
Hydrocarbons	H/C ratio	Density (g/ml)	Calc. ΔH_f (Kcal/mole)	Calc. Isp (sec)
RP-1	1.9	0.80	-5.76	300.0
Quad	1.14	0.98	72.2	307.0
BCP	1.33	0.85	76.1	312.5
AFRL-1	1.2	0.77	64.0	311.3
AFRL-2	1.25	0.87	73.4	307.2
AFRL-3	1.0	0.93	123.6	307.2
AFRL-4	1.0	-	129.6	321.4
AFRL-5	1.33	0.80	56.3	308.7



Results

Synthetic Sequence of BCP





Characterization of BCP

Physical properties

B.P. = 101 °C

M.P. = -12 °C

F.P. = -6.4 °C

Density = 0.8454 g/ml

ΔH_f (exp.) = 67.4 kcal/mole

ΔH_f (calc.) = 76.1 kcal/mole

Hazardous properties

Zero card gap (negative)

Drop test > 200 kg/cm

Friction test 133 newton

Toxicity

(Inhalation LC50)

1.95 mg/L

Adiabatic Compression(psi)

3000

Neg.



Is BCP Hypergolic?

- **Qualitative Test**

- BCP is found to be hypergolic using nitrogen tetroxide (NTO). Spontaneous reaction with visible flame.
- Hypergolic with inhibited red fuming nitric acid (IRFNA) as oxidizers. (Darren M. Thompson, U.S. Army missile command).

- **Ignition Delay**

- The work is in progress under SBIR phase-1 with TDA Research, Inc.



Synthesis of AFRL-1

- Two steps synthesis
- Involves readily available materials
- Yield in both steps is $> 90\%$



Characterization of AFRL-1

Physical Properties

B.P. = 52- 55 °C

Density = 0.77 g/ml

ΔH_f (Exp.)= 67.4 Kcal/mole

ΔH_f (Calc.)= 64.0 Kcal/mole

Hazardous Properties

“0” card gap (Negative)

Liq. Impact test > 200 Kg-cm

Friction Test 78 Newtons

Adiabatic Compression (psi)

3000

Neg.



Synthesis of AFRL-3

- One step synthesis from AFRL-1.
- Requires oxidative coupling of AFRL-1.
- Yield is 92 %.



Characterization of AFRL-3

Physical Properties

B.P. = 102 °C

M.P. = -13 °C

Density = 0.93 g/ml

ΔH_f (Calc.) = 123.6 kcal/mole

ΔH_f (Exp.) = 117.0 kcal/mole

Hazardous Properties

- “0” card gap (negative)
- Liq Impact test <20 kg-cm
- Friction Test = 64.8 Newton

Adiabatic Compression(psi)

500	Neg.
2000	Neg.
3000	Neg.



Synthesis of AFRL-5

- Higher homologue of AFRL-1
- Two step synthesis
- Yield in both steps is greater than 90 %



Characterization of AFRL-5

Physical properties

B.P. = 78 °C

M.P. = -92.8 °C

Density = 0.7957 g/ml

ΔH_f (Exp.) = 50.39
kcal/mole

ΔH_f (Calc.) = 56.3 kcal/mole

Hazardous properties

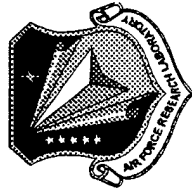
“0”card gap (TBD)

Liq. Impact Test > 200 kg-cm

Friction Test = 43.12 newton

Adiabatic Compression (psi)

3000	Neg.
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Accomplishments (FY 00)

- Delivered four hydrocarbons to NASA/Marshall.
 - Cyclopropyl acetylene (AFRL-1).
 - Bicyclopropylidene
 - Quadricyclane
 - 1,7-Octadiyne
- Synthesized two advanced hydrocarbons (AFRL-1 & AFRL-3) at bench-scale level.
- 200 gm of AFRL-3 was synthesized in the laboratory.



Planned Efforts of Fiscal Year 2001 (Technical)

- To continue exploring bench scale synthesis of advanced hydrocarbon (AFRL-4).
- Evaluate physical & hazardous properties of AFRL-4 & AFRL-2.



Alliances

- **Industry**
 - Boeing
 - TRW
 - Kistler
 - Aerojet
- **NASA**
 - Marshall
 - Glenn
- **DOD**
 - Navy- China Lake
 - Army- Huntsville



Team Efforts

Research

- Suresh C. Suri
Michael Tinnirello
Jacob Marcischak

Theoretical Efforts

- Jeffrey Mills

Physical Properties

- Paul Jones, JoAnne Larue,
Jeff Yinn

Hazardous Properties

- Tommy W. Hawkins,
Adam Brand, Milton
Mckay, Ismail Ismail



Acknowledgement

Financial Support

- Air Force Office of Scientific Research (AFOSR)
- National Aeronautics and Space Administration (NASA)/MSFC