Combustion Kinetics Databases for Real Fuels

Jeffrey A. Manion

National Institute of Standards and Technology
Physical and Chemical Properties Division
Gaithersburg MD 20899

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Chicago, IL
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Structure of Talk

PART 1: Background & Context: NIST Mission & Role in Energy

PART 2: Results of NIST Real Transportation Fuels Workshop

PART 3: NIST Real Fuels Project: Modernizing Combustion Databases

NIST Mission

- To develop and promote measurement, standards, and technology to enhance productivity, facilitate trade, and improve the quality of life.

- Provide, when requested, measurements, data, and standards to support the missions of other agencies.

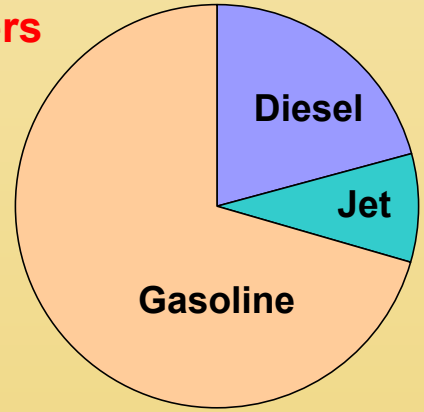
Energy Production for Transportation - National Impacts

Year 2000

731 Billion Liters

$272 Billion

Liquid Fuels



Year 2000 *	Number of Employees	Payroll	Value of shipments
Motor Vehicle Mfg.	230,525	14.6 B	239.4 B
Transportation Equipment Mfg.	1,839,281	86.9 B	638.7 B

Monetary Importance:

- Economic Competitiveness
- Energy Self-Sufficiency
- Green House Gas Trading Credits
- Healthcare costs

Quality of Life (Pollution Effects):

- Heart/Lung Disease
- Environmental Degradation
- Global Warming
- Premature death

*** "*Statistics for Industry Groups and Industries: 2000*", Publication M00(AS)-1, U.S. Census Bureau, Economics and Statistics Administration, U.S. Department of Commerce, 2002.**

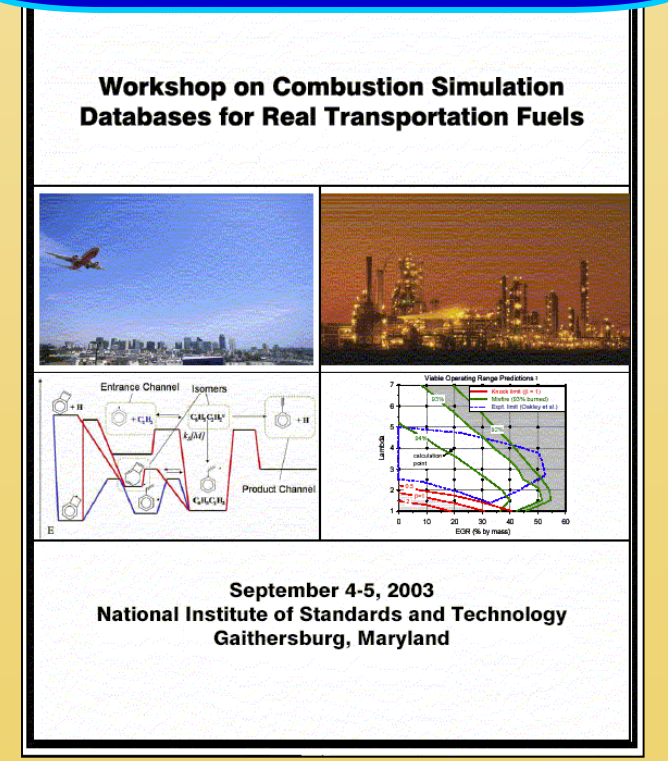
NIST Sponsored Workshop

***Workshop on Combustion Simulation Databases for Real Transportation Fuels*, NIST, Gaithersburg, MD, September 4-5, 2003.**

Approximately 60 Scientists

- ❑ **Industry**
- ❑ **Academia**
- ❑ **Government Agencies**

Report Available Today



Purpose:

Help NIST and community assess data requirements for modeling combustion of transportation fuels and recommend plans for developing reference databases and chemical kinetic models.

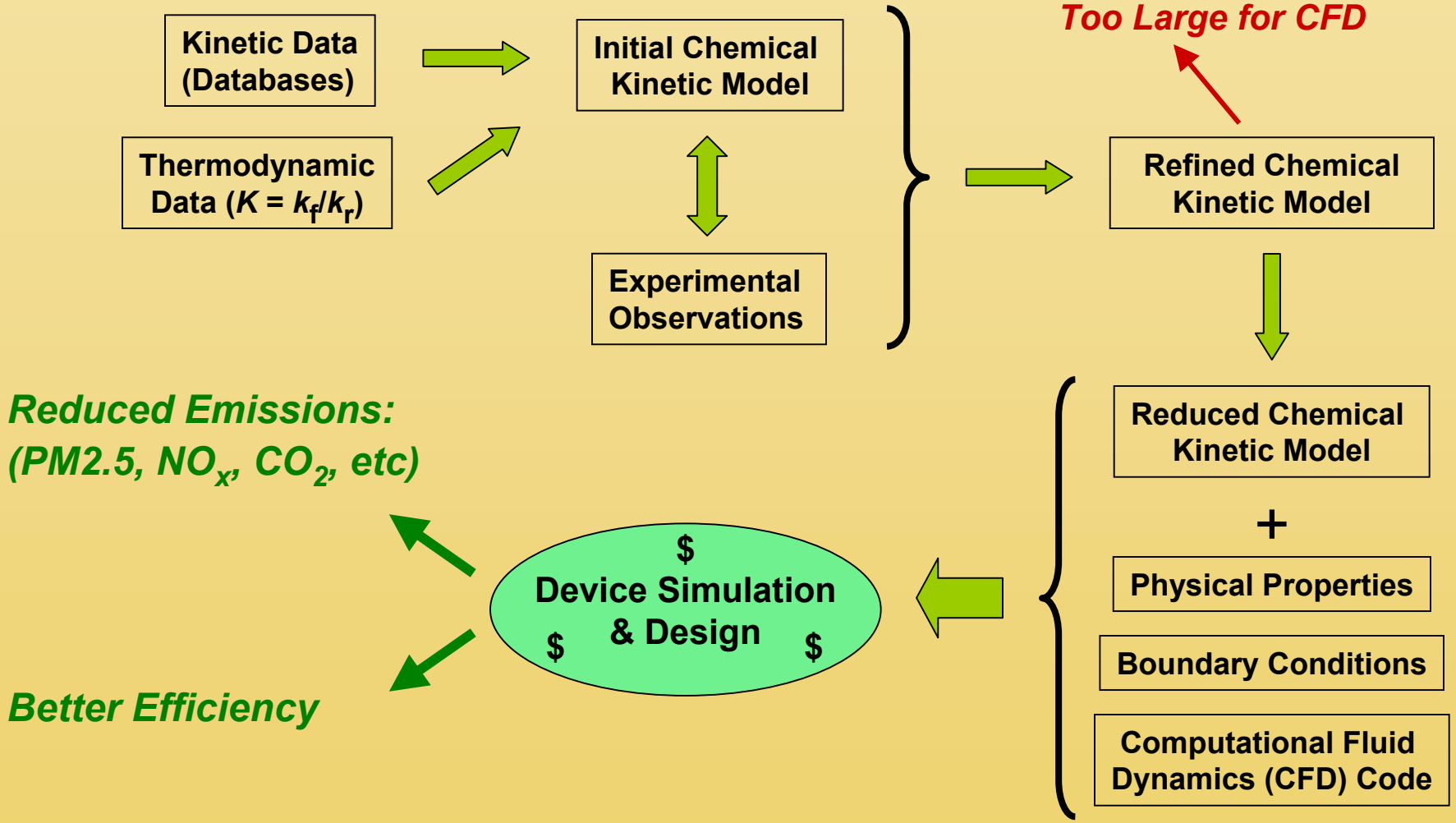
Workshop Findings

Simulations combining CFD and chemical kinetic models are predictively useful at present and their role in device design will continue to increase in the future.

Types of Needs Identified (chemistry):

- **Existence & Quality of Data on Real Fuels**
- **Infrastructural – Ability to rapidly find, share and use information.**

Vision: The Application of Kinetics Databases to Combustion



Some Current Issues – Combustion Modeling

Multiple Models of Many Systems Exist – But Are Difficult To Compare.

Model 1

1800 Reactions
360 Species

Model 2

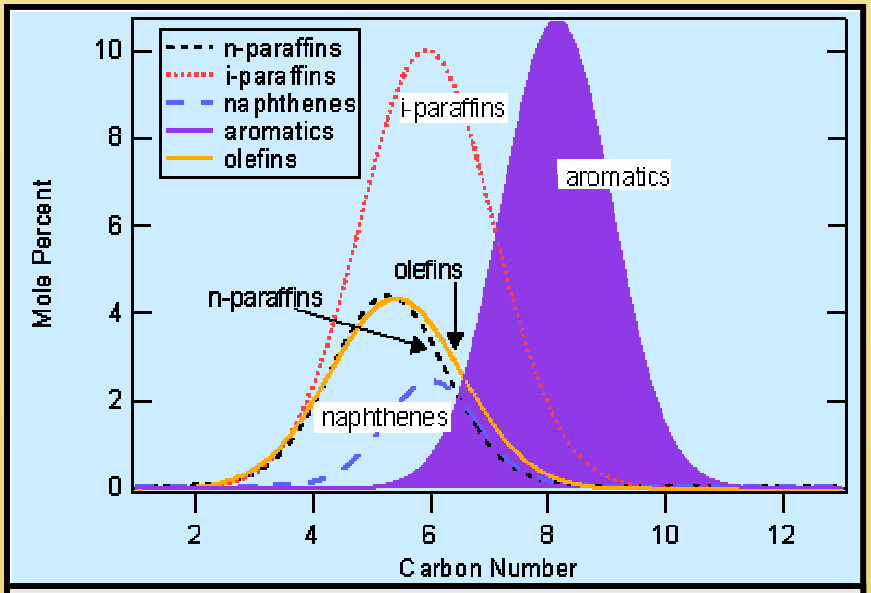
2200 Reactions
405 Species

- Reaction sets are different
- Rate constants are different
- Thermodynamic sets are different
- Species are identified by different strings (understandable only to creator)
- Data often not traceable – no reference or reference is not original source
- No common validation experiments

Dilemma: How do you choose?
How do you begin to compare, to improve?
How much TIME will it take?

Some Current Issues – Modeling Real Fuels I

Real Fuels are complex mixtures with varying compositions – How to Develop Useful Kinetic Models?



Composition of Gasoline. *Adapted from J. Farrell, Exxon Mobil Corp.*

- 100's of Compounds
- Relatively few classes

Surrogate Fuels Concept

Surrogate Fuels – Workshop Consensus

Preliminary Suggestions

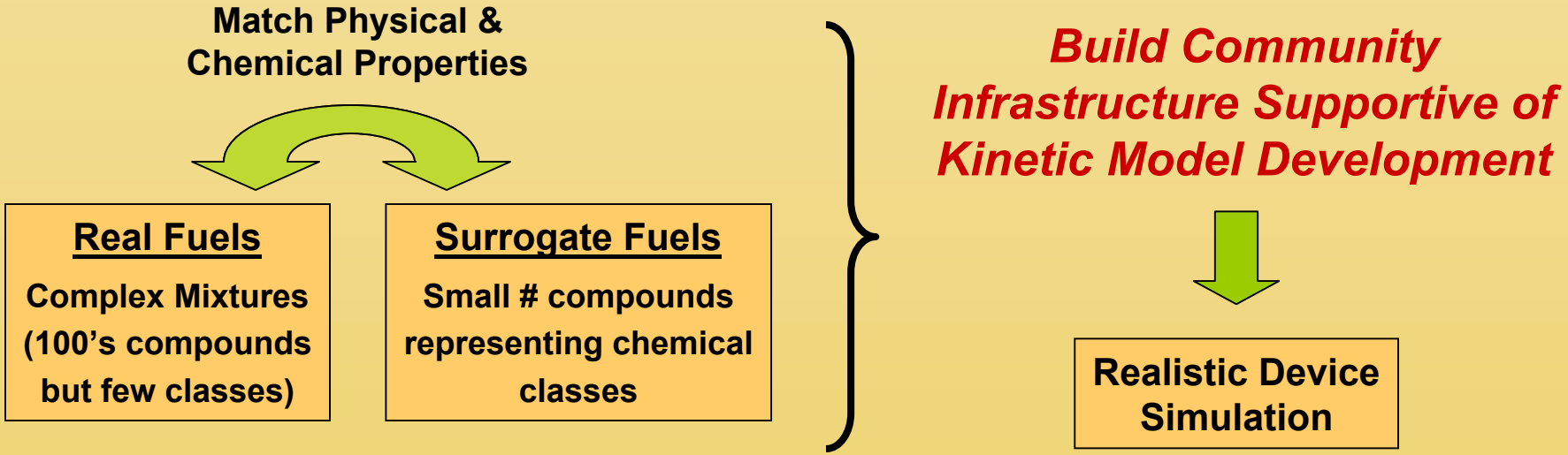
Chemical Class	Model Compound(s)
Normal Paraffins	Heptane, Decane, Hexadecane
Iso-paraffins	*iso*-octane
Cycloparaffins	Methylcyclohexane
Olefinic Species	1-pentene
Single-Ring Aromatics	Toluene, Xylenes
Multi-Ring Aromatics	1-methylnaphthalene

Working Hypotheses:

- **Surrogates for gasoline, diesel and aviation fuels can be composed of same model compounds (in different proportions).**
- **Probably several different surrogates needed for each fuel.**
- **Single database useful to all.**

NIST Real Fuels Project - Concept

NIST "Real Fuels" Project: A collaborative effort designed to *enable* the combustion of liquid transportation fuels (diesel, gasoline, aviation) to be realistically simulated for device design purposes.



Workshop on Combustion Simulation Databases for Real Transportation Fuels, National Institute of Standards and Technology, Gaithersburg, MD, September 4-5, 2003.

Components of NIST Real Fuels Project

Experimental:

- Surrogate fuels concept
- Experiments to fill knowledge gaps

Infrastructural:

- Design intelligent data structures for combustion information
- Create web-accessible data warehouse for combustion modeling
- Promote collaborative paradigm for development of chemical kinetic models of combustion systems

Components of NIST Real Fuels Project

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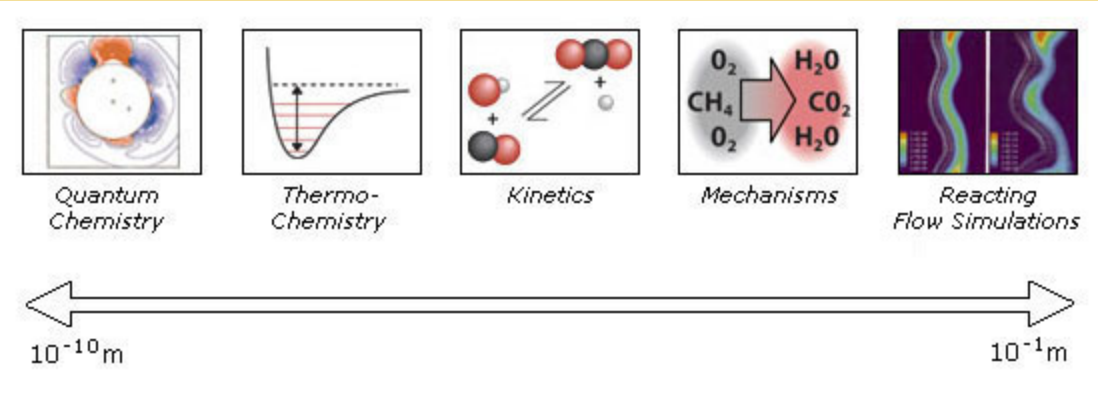
Won't solve all problems, but can:

- take key steps
- lay the foundation for systematic progress

Partnering: NIST – PrIMe – CMCS Collaboration

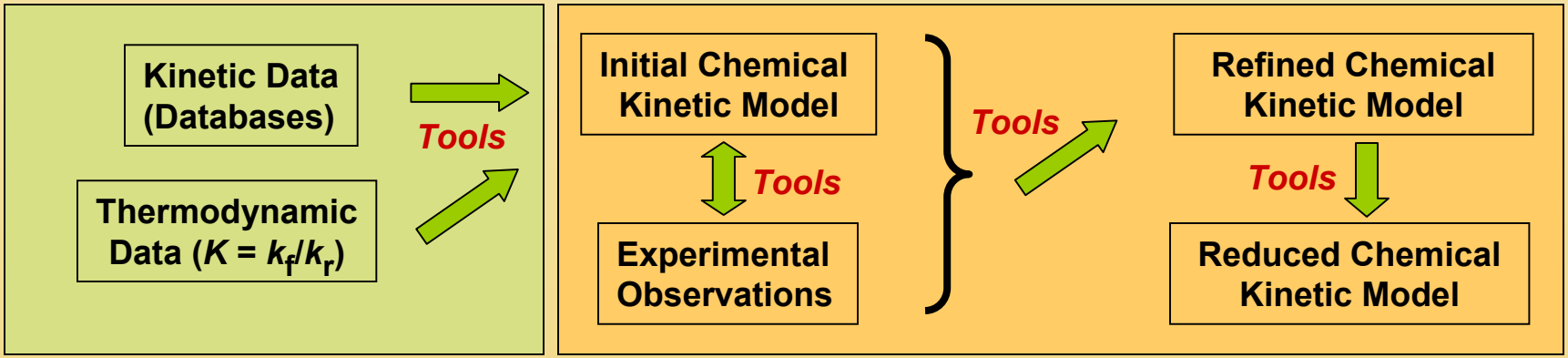
Collaboratory for Multi-scale Chemical Science (CMCS): DOE funded ***computer science*** project whose goal is to to enhance chemical science research by developing an adaptive informatics infrastructure. Larry Rahn, Sandia - CMCS.org



Process Informatics Model (PrIMe): A community effort to develop predictive reaction models for combustion. The goal is to convert model building into a science, automate the methodology, and provide the results to the User in a prompt and convenient format. (Outgrowth of GRI-Mech) Michael Frenklach - UCB

Sandia National Laboratories · Pacific Northwest National Laboratory (Operated by Battelle for the U.S. Department of Energy) · Argonne National Laboratory · Los Alamos National Laboratory · NIST National Institute of Standards and Technology · MIT Massachusetts Institute of Technology · Berkeley

NIST – PrIMe – CMCS Collaboration



NIST/PrIMe Data Warehouse:

- All kinetic data on elementary reactions relevant to combustion (*NIST Gas Kinetics, GRI Mech*)
- Relevant thermodynamic data
- Global kinetic data for model validation.

PrIMe Process (Vision):

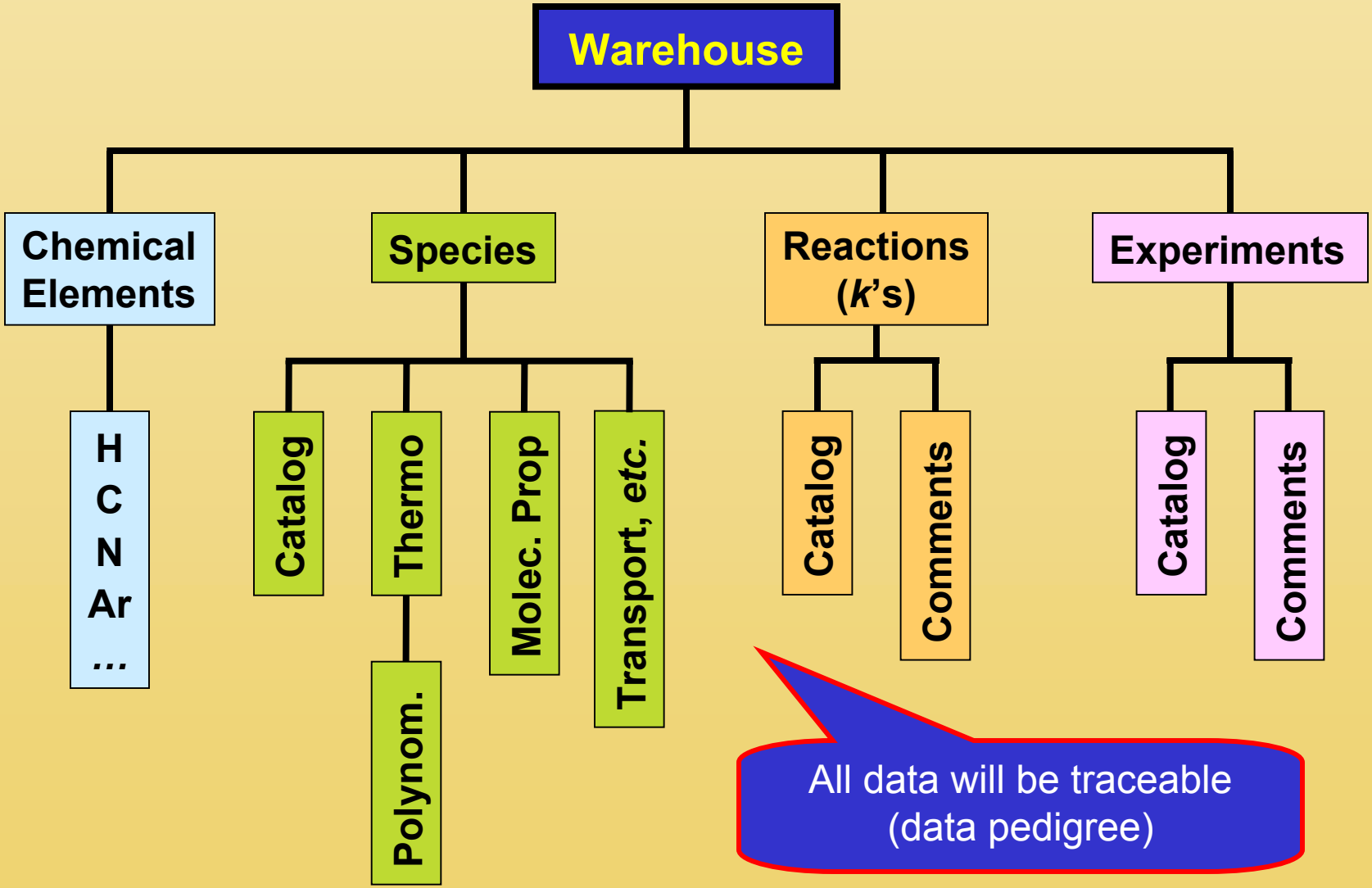
- Community-based evaluation of Warehouse Data → "Best" values with uncertainties.
- Selected set of "Best" validation experiments for combustion models
- Set of Community Tools for "on-the fly" generation of "Best Current Kinetic Model"

CMCS: Implementation of Computer Science Infrastructure.

Underlying Principles of NIST/PrIMe Warehouse

- Internet-based
- Open Membership
- Accessible thru CMCS Portal

Organization of NIST/PrIMe Data Warehouse



NIST/PrIMe Data Warehouse – Ongoing Steps

Integrate Existing Kinetic & Thermodynamic Information:

- ❑ NIST Gas Phase Kinetics Database
- ❑ GRI Mech 3.0
- ❑ Leeds Combustion Mechanism (anticipated)
- ❑ Other?

Develop Electronic Data Entry Forms:

- ❑ Enable contributions as data is produced
- ❑ Forms ensure easy transfer & minimum information standards

NIST Real Fuels Website

Under Construction

http://kinetics.nist.gov/RealFuels

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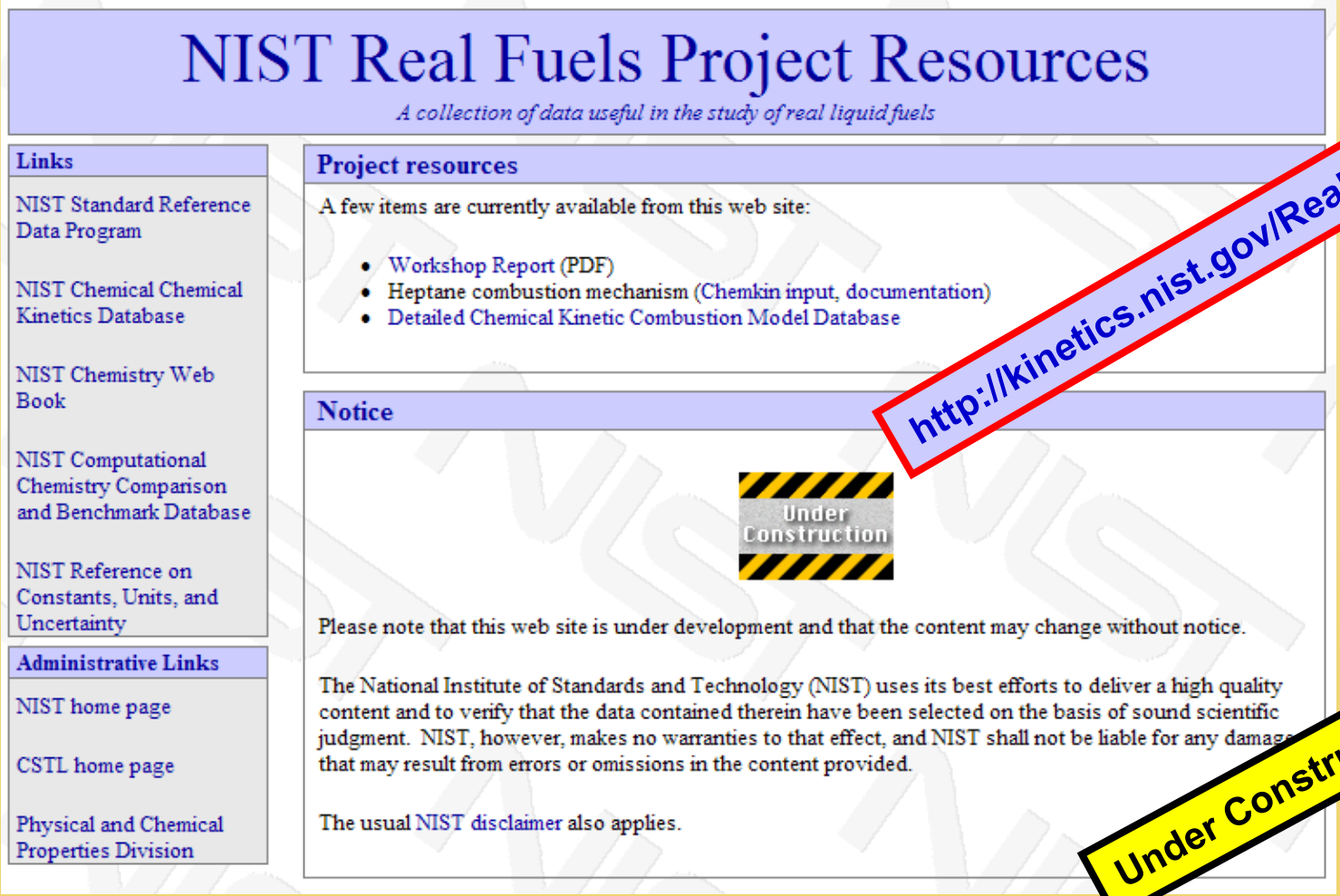
- Information Specific to Real Fuels (TBD)
- Archival Mechanisms
- Relational Mechanism Database
  - Deposit will be via data entry forms
- Will merge with or link to NIST/PrIMe Data Warehouse

NIST Real Fuels Website



NIST Chemical Kinetic Model Database

NIST DETAILED CHEMICAL KINETIC COMBUSTION MODEL DATABASE

OVERVIEW	MODELS	REACTIONS	SPECIES	BIBLIOGRAPHY

Models	• Archival "flat file" listings of detailed chemical kinetic models with brief descriptions and links to papers, validation experiments, and related models • Dynamical "relational" listings of detailed chemical kinetic models with links to species molecular properties, primary thermochemical data, chemical reaction rate expressions, and bibliographic information, and other related information
Reactions	• Search, manipulate, and compare individual reactions or reactions by class for specific detailed kinetic models or among models or build a model based on recommended values
Species	• Molecular identifiers such as CASNO, chemical names, etc. • Molecular structures and chemical information such as structural/chemical formulae, SMILES strings, NIChI identifiers, MDL mol files, chemical classes, etc. • Molecular properties such as experimental or calculated structures, vibrational frequencies, etc. • Thermochemical data DfHo, So, Cp(T); NASA format polynomial fits, etc.
Bibliography	• Bibliographic information supporting models, reactions, and species

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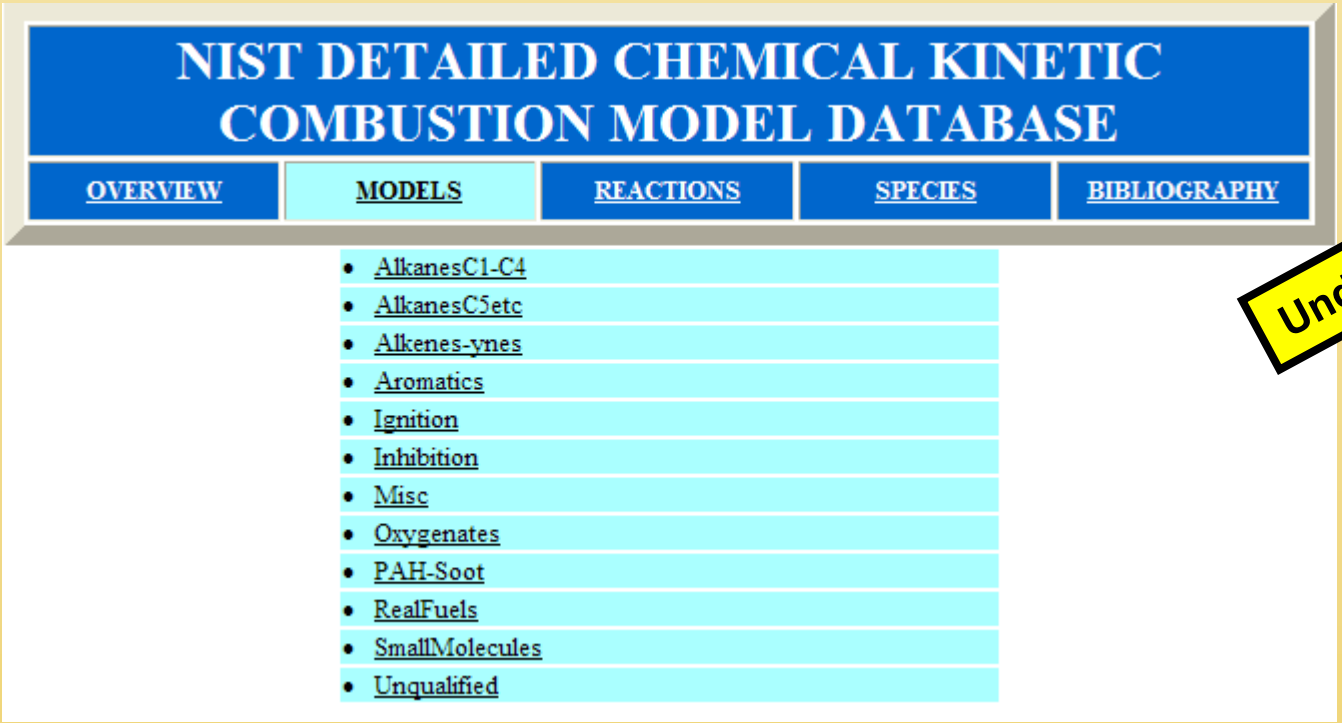
NIST Real Fuels Website – Model Search



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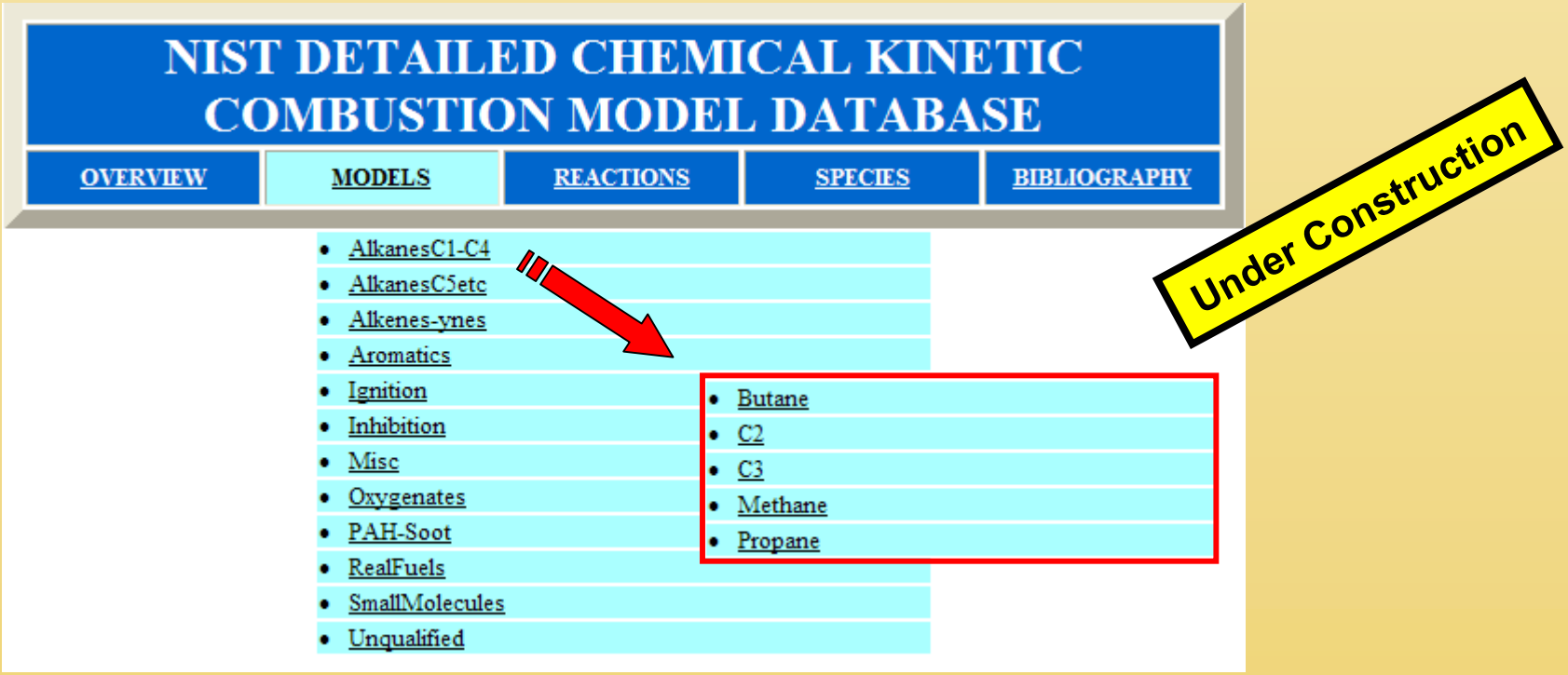

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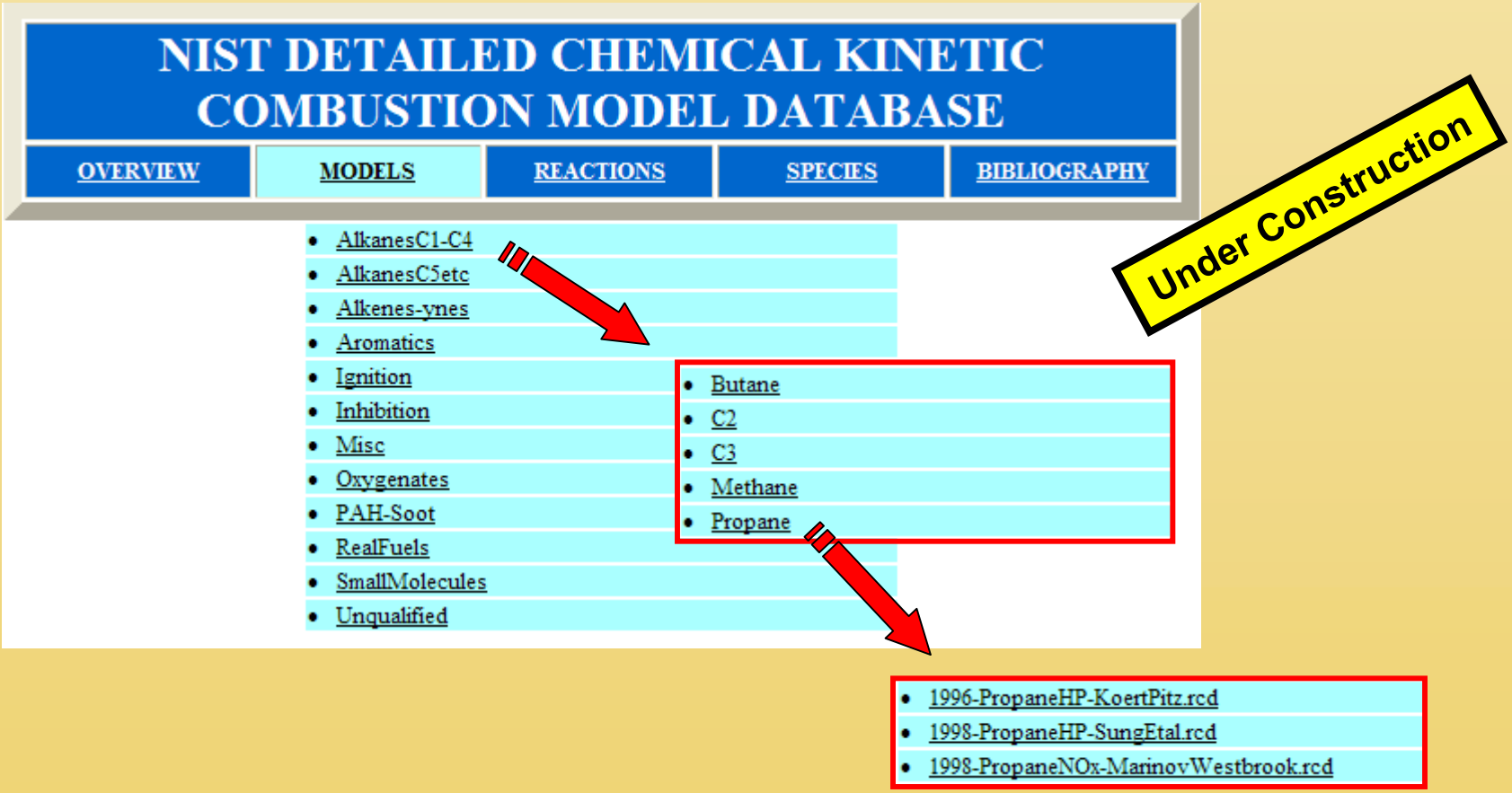

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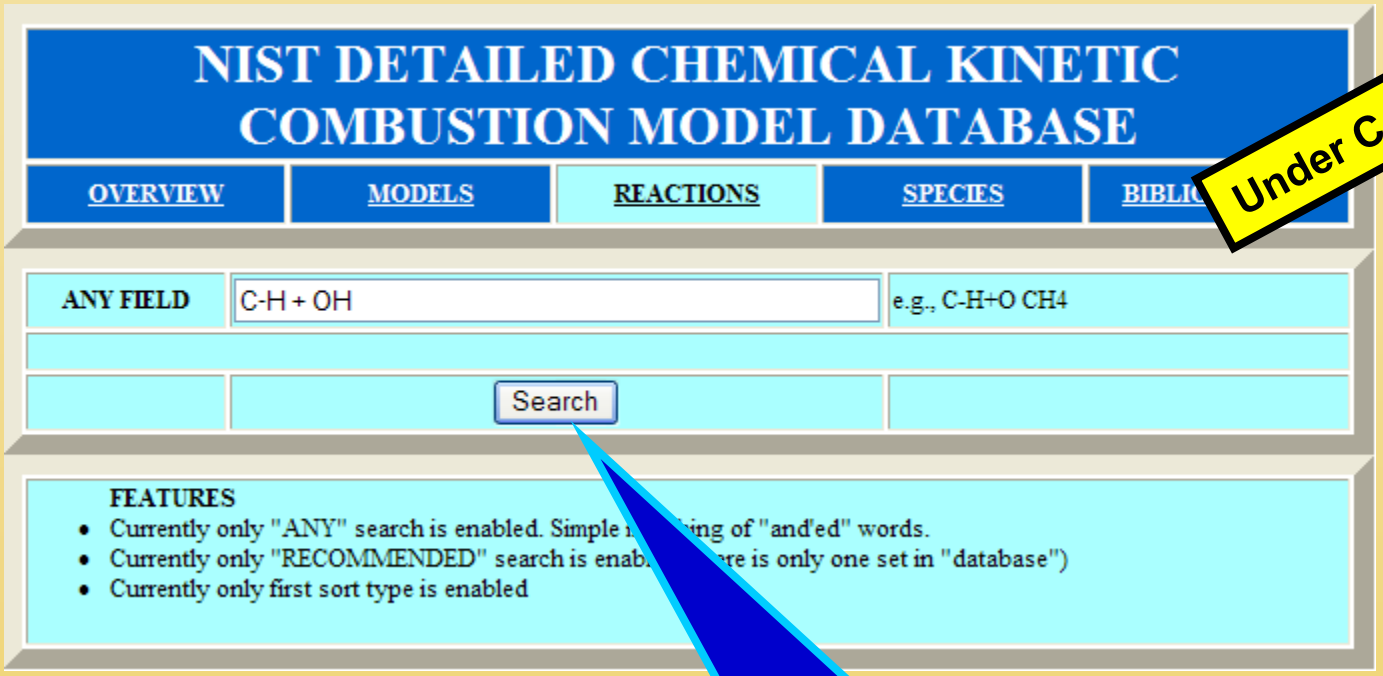
NIST Real Fuels Website – Reaction Search



http://kinetics.nist.gov/RealFuels

NIST Real Fuels Website – Reaction Class

ıssNo	Reaction Class	Valence	Notation	Example	Reaction Example
)0	**UNIMOLECULAR**				
)0	**Radical Elimination**				
)1	Bond Fission	Full	R-X	C-H	$C_2H_6 \rightarrow C_2H_5 + H$
11	Beta Scission	Radical	R.S-X	C.C-H	$C_2H_5 \rightarrow C_2H_4 + H$
21	Beta Fission	Ylidene	R:S-X	C:C-H	$CH_3CH: \rightarrow C_2H_3 +$
)0	**Molecular Elimination**				$\rightarrow$
)1	1,1-Elimination	Full	R-XY	C-HH	$C_2H_6 \rightarrow C_2H$
)2	1,2-Elimination	Full	RS-XY	CC-HH	$C_2H_6 \rightarrow CH_3CH: + H_2$
)3	1,3-Elimination	Full	RS-XY(3)	CC-CH(3)	1,3-Butadiene $\rightarrow C_2H_4 + C_2H_2$
)4	1,4-Elimination	Full	RS-XY(4)	CC-CH(4)	Cyclohexene $\rightarrow$ 1,3-Butadiene + C_2H_4
11	1,1-Elimination	Radical	R.S-XY	O.C-HF	$CHF_2O^* \rightarrow CFO + HF$
12	1,2-Elimination	Radical	RS.-XY	OC.-HF	$^*CF_2OH \rightarrow CFO + HF$
)0	**BIMOLECULAR**				
)0	**Metathesis**				
)1	Abstraction	Full + Rad	R-X+Y	C-H+C	$C_2H_6 + CH_3^* \rightarrow C_2H_5^* + CH_4$
11	Disproportionation	Rad + Rad	R.S-X+Y	C.C-H+C	$C_2H_5^* + CH_3^* \rightarrow C_2H_4 + CH_4$
)0	**Substitution/Displacement**				
)1	Displacement	Full + Full	R+X:-Y	Al+O:-C	$Al(CH_3)_3 + H_2O \rightarrow Al(OH)(CH_3)_2 + CH_4$
11	Substitution	Full + Rad	R+X-Y	Al+H-C	$Al(CH_3)_3 + H \rightarrow AlH(CH_3)_2 + CH_3^*$
)0	**Stepwise Bimolecular**				
11	Addition//Beta Scission	Full + Rad	R+S//R.S-X	C+C//C.C-Cl	$CH_2{=}CHCl + H \rightarrow CH_2{=}CH_2 + Cl$

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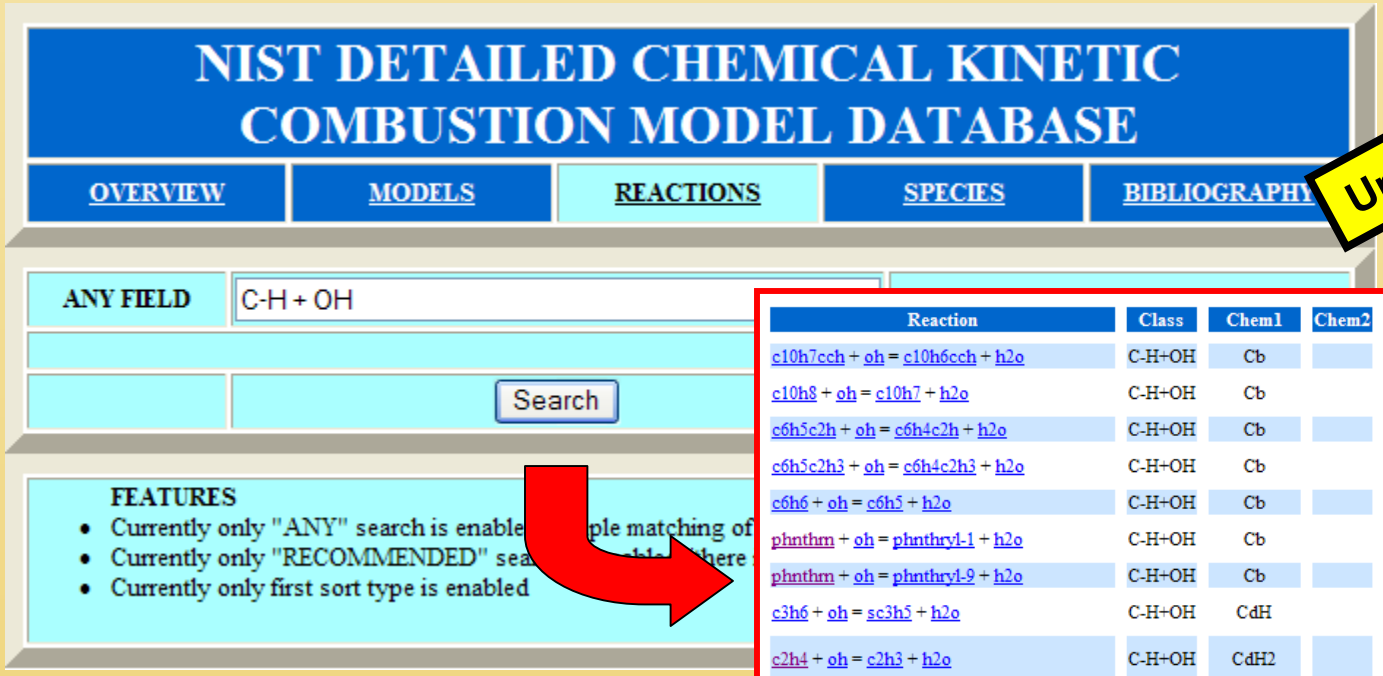
NIST Real Fuels Website – Reaction Search



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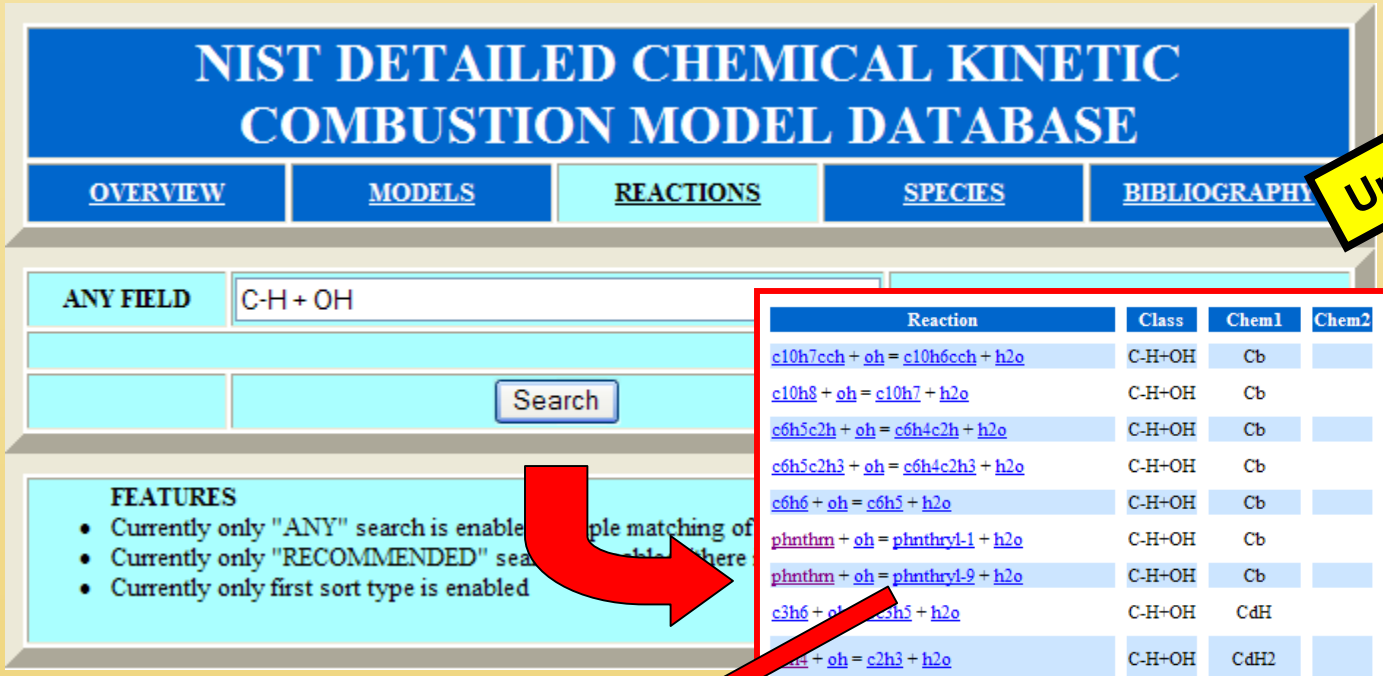
Reaction	Class	Chem1	Chem2	A	b	E	SQUIB
c10h7cch + oh = c10h6cch + h2o	C-H+OH	Cb		1.63E+08	1.42	1454	1996MAR/PIT211-287
c10h8 + oh = c10h7 + h2o	C-H+OH	Cb		2.44E+08	1.42	1454	1996MAR/PIT211-287
c6h5c2h + oh = c6h4c2h + h2o	C-H+OH	Cb		1.63E+08	1.42	1454	1996MAR/PIT211-287
c6h5c2h3 + oh = c6h4c2h3 + h2o	C-H+OH	Cb		1.63E+08	1.42	1454	1996MAR/PIT211-287
c6h6 + oh = c6h5 + h2o	C-H+OH	Cb		1.63E+08	1.42	1454	1992BAU/COB411-429
phnthm + oh = phnthryl-1 + h2o	C-H+OH	Cb		2.17E+08	1.42	1454	1996MAR/PIT211-287
phnthm + oh = phnthryl-9 + h2o	C-H+OH	Cb		5.43E+07	1.42	1454	1996MAR/PIT211-287
c3h6 + oh = sc3h5 + h2o	C-H+OH	CdH		1.11E+06	2	1451	1991TSA221-273
c2h4 + oh = c2h3 + h2o	C-H+OH	CdH2		2.02E+13	0	5936	1992MEL/MIL621-628 (check)
ch2chchch2 + oh = ch2chchch + h2o	C-H+OH	CdH2		2.00E+07	2	5000	1992MEL/MIL621-628 (check)
ch2chcch + oh = hcchcch + h2o	C-H+OH	CdH2		7.50E+06	2	5000	1992MEL/MIL621-628 (check)
c3h6 + oh = pc3h5 + h2o	C-H+OH	CdH2		2.11E+06	2	2778	1991TSA221-273
ac3h4 + oh = h2ccch + h2o	C-H+OH	CdH2-Ca		1.00E+07	2	1000	1999MAR183-220
ch3chcch2 + oh = ch3ccch2 + h2o	C-H+OH	CdH-Ca		1.00E+07	2	2000	
c10h7c2h3 + oh = c10h7cch2 + h2o	C-H+OH	CdH-Cb		1.00E+07	2	2000	1996MAR/PIT211-287
c6h5c2h3 + oh = c6h5cch2 + h2o	C-H+OH	CdH-Cb		1.00E+07	2	2000	1996MAR/PIT211-287
ch2chchch2 + oh = ch2chcch2 + h2o							

http://kinetics.nist.gov/RealFuels

NIST Real Fuels Website – Reaction Search



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c10h7cch + oh = c10h6cch + h2o	C-H+OH	Cb		1.63E+08	1.42	1454	1996MAR/PIT211-287
c10h8 + oh = c10h7 + h2o	C-H+OH	Cb		2.44E+08	1.42	1454	1996MAR/PIT211-287
c6h5c2h + oh = c6h4c2h + h2o	C-H+OH	Cb		1.63E+08	1.42	1454	1996MAR/PIT211-287
c6h5c2h3 + oh = c6h4c2h3 + h2o	C-H+OH	Cb		1.63E+08	1.42	1454	1996MAR/PIT211-287
c6h6 + oh = c6h5 + h2o	C-H+OH	Cb		1.63E+08	1.42	1454	1992BAU/COB411-429
phnthm + oh = phnthryl-1 + h2o	C-H+OH	Cb		2.17E+08	1.42	1454	1996MAR/PIT211-287
phnthm + oh = phnthryl-9 + h2o	C-H+OH	Cb		5.43E+07	1.42	1454	1996MAR/PIT211-287
c3h6 + oh = pc3h5 + h2o	C-H+OH	CdH		1.11E+06	2	1451	1991TSA221-273
ac3h4 + oh = c2h3 + h2o	C-H+OH	CdH2		2.02E+13	0		1992MEL/MIL621-628 (check)
ch2chchch2 + oh = ch2chchch + h2o				2.00E+07	2	5000	1992MEL/MIL621-628 (check)
oh = hcchcch + h2o	C-H+OH	CdH2		7.50E+06	2	5000	1992MEL/MIL621-628 (check)
c3h6 + oh = pc3h5 + h2o	C-H+OH	CdH2		2.11E+06	2	2778	1991TSA221-273
ac3h4 + oh = h2ccch + h2o	C-H+OH	CdH2-Ca		1.00E+07	2	1000	1999MAR183-220
ch3chcch2 + oh = ch3ccch2 + h2o	C-H+OH	CdH-Ca		1.00E+07	2	2000	
c10h7c2h3 + oh = c10h7cch2 + h2o	C-H+OH	CdH-Cb		1.00E+07	2	2000	1996MAR/PIT211-287
c6h5c2h3 + oh = c6h5cch2 + h2o	C-H+OH	CdH-Cb		1.00E+07	2	2000	1996MAR/PIT211-287
ch2chchch2 + oh = ch2chcch2 + h2o							

Species & Bibliographic Information Links

http://kinetics.nist.gov/RealFuels

NIST Real Fuels Website – Species Form

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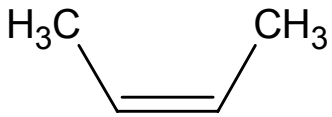
DESCRIPTION					
Title	(Z)-2-Butene				more
Identifiers	590-18-1	CAS-yes			more
Names/Symbols	but2ene-z	(Z)-2-Butene			more
Structural Representations					more
Composition	52	C4H8	C/C=C\C		more
Chemical	Alkylalkenes				more
Related	2-Butene	(E)-2-Butene	n-Butane	2-Butenyl	more
Databases	Webbook ; NISTKinetics ; CCCBDB; GRIMech ; RealFuels ; Burcat ; Chemkin				more
Notes					more
DATA					
Physical	more	Thermochemical	more	Quantum Calc	more
Mechanistic	more	Reactions	more	Kinetics	more

http://kinetics.nist.gov/RealFuels

NIST Real Fuels Website – Species Info Links

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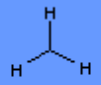
Heat of Formation: CH3



$\Delta_f H^0_{298}$	Uncert	Units	SQUIB	Method	Data Type
145.7	0.0	kJ/mol	1985CHA/DAV1-1856	Review	Review
146.9	0.0	kJ/mol	1983GAR/LIS	Review	Review
146.9	1.0	kJ/mol	1995BUR/MCB1	Review	Review
-148.3	0.0	kJ/mol	1998UNP/DAT9999	CBS-Q	Theory/abinitio
143.1	0.0	kJ/mol	1998CUR/RAG7764-7776	G3MP2	Theory/abinitio
146.8	0.8	kJ/mol	1982MCM/GOL493-532	Review	Review
146.4	0.4	kJ/mol	1994BER/ELL2744-2765	Review	Review
147.0	1.0	kJ/mol	1996TSA	review	Review
132.6	0.0	kJ/mol	1997CUR/RAG1063	B3LYP/6-311+G(3df,2p)	Theory/DFT
142.3	0.0	kJ/mol	1998CUR/RAG7764-7776	G3	Theory/abinitio
146.4	0.0	kJ/mol	1992CUR/CAR9030-9034	G2(QCI)	Theory/abinitio
154.0	0.0	kJ/mol	1991CUR/RAG7221-7230	G1	Theory/abinitio
149.4	0.0	kJ/mol	1997CUR/RAG1063	G2MP2(SVP)	Theory/abinitio
134.3	0.0	kJ/mol	1997CUR/RAG1063	B3PW91/6-311+G(3df,2p)	Theory/DFT
146.6	0.3	kJ/mol	1999RUS/LIT8625-8633	thermochemical network	Review
146.0	0.0	kJ/mol	1992ATK/BAU1125-1568	Review	Review
147.7	2.5	kJ/mol	1991NIC/VAN9890-9896	kinetic/CH3+HBr=CH4+Br	Experiment/kinetic

http://kinetics.nist.gov/RealFuels

NIST Real Fuels Website – Species Search

NIST DETAILED CHEMICAL KINETIC COMBUSTION MODEL DATABASE

OVERVIEW | MODELS | REACTIONS | SPECIES | BIBLIOGRAPHY

Under Construction

Browse

Chemical Classes

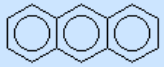
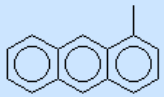
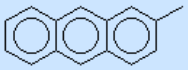
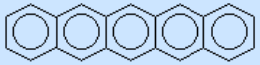
Search

PAHChI

PPP

Search

PAH Results

Base Class	Formula	Species	CASNO	Structural Image	PAHChI
Anthracenes/	C14H10	Anthracene	120127		PPP
Anthracenes/	C15H12	1-Methylanthracene	610480		PPP(1C)
Anthracenes/	C15H12	2-Methylanthracene	613127		PPP(2C)
Anthracenes/	C18H12	Naphthacene	92240		PPPP
Anthracenes/	C22H14	Pentacene	135488		PPPPP

http://kinetics.nist.gov/RealFuels

Overall Goals I:

Goal is to organize and integrate the data.

Databases and data structures should facilitate *use* of the data

Overall Goals II

Fundamental Science

Applied Science

Feedback and interaction through data exchange benefits all communities

Future Directions

Additional Workshops – Potential Topics:

- Development of community-led data evaluation process
- Global experimental kinetic data for model validation (flame speeds, flame profiles, etc.)
- Specific topical areas (e.g. soot formation, kinetics of "cool flames" region, surrogate fuels, etc.)
- Development/Incorporation of community science tools
- *Ab initio* data
- Other?

NIST Real Fuels Project - People

NIST Staff:

- Jeff Manion (Project Leader)
- Wing Tsang
- Don Burgess
- Jeff Hudgens
- Tom Allison

NRC Post Doctoral Fellows:

- Dave Matheu (MIT - Advisor Bill Green)
- W. Sean McGivern (Texas A&M – Adv. Simon North)
- Michael Donovan (Univ. of Michigan – Adv. Margaret Wooldridge)

Various Internal Collaborations (BFRL, Comp. Chemistry, Webbook)

Final Comments

- Partners are crucial to infrastructure development.
- Process is under development (input welcome)
- NIST seeks to be inclusive and support (not dictate) community efforts.