LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-CONF-408237

Development of Detailed Kinetic Models for Fischer-Tropsch Fuels

C. K. Westbrook, W. J. Pitz, H.-H. Carstensen, A. M. Dean

October 29, 2008

Spring 2009 National Meeting & Exposition
Salt Lake City, UT, United States
March 22, 2009 through March 26, 2009

Disclaimer

Development of Detailed Kinetic Models for Fischer-Tropsch Fuels

Charles K. Westbrook, William J. Pitz*, Hans-Heinrich Carstensen†, and Anthony M. Dean†*

* Physical and Life Sciences Directorate, Lawrence Livermore National Lab, Livermore, CA 94551
†Chemical Engineering Department, Colorado School of Mines, Golden, CO 80401

Introduction

Fischer-Tropsch (FT) fuels can be synthesized from a syngas stream generated by the gasification of biomass. As such they have the potential to be a renewable hydrocarbon fuel with many desirable properties. However, both the chemical and physical properties are somewhat different from the petroleum-based hydrocarbons that they might replace, and it is important to account for such differences when considering using them as replacements for conventional fuels in devices such as diesel engines and gas turbines. FT fuels generally contain iso-alkanes with one or two substituted methyl groups[1,2] to meet the pour-point specifications. Although models have been developed for smaller branched alkanes such as isooctane[3], additional efforts are required to properly capture the kinetics of the larger branched alkanes. Recently, Westbrook et al.[4] developed a chemical kinetic model that can be used to represent the entire series of n-alkanes from C_1 to C_{16} (Figure 1). In the current work, the model is extended to treat 2,2,4,4,6,8,8-heptamethylnonane (HMN), a large iso-alkane. The same reaction rate rules used in the iso-octane mechanism were incorporated in the HMN mechanism. Both high and low temperature chemistry was included so that the chemical kinetic model would be applicable to advanced internal combustion engines using low temperature combustion strategies. The chemical kinetic model consists of 1114 species and 4468 reactions. Concurrently with this effort, work is underway to improve the details of specific reaction classes in the mechanism, guided by high-level electronic structure calculations. Attention is focused upon development of accurate rate rules for abstraction of the tertiary hydrogens present in branched alkanes and properly accounting for the pressure dependence of the β-scission, isomerization, and R + O_2 reactions.

Results

2,2,4,4,6,8,8-heptamethylnonane. Currently, there are no experimental data available on neat HMN to validate the predictions of the chemical kinetic model. Instead the results of the HMN chemical kinetic model were compared to other alkane fuel predictions and experiments. In Figure 1, the autoignition properties of HMN are compared to n-alkanes and an iso-alkane, iso-octane. It is seen that the ignition delay times of HMN lie between large n-alkanes and iso-octane at low temperatures and are nearly the same as the other fuels at high temperatures. This low temperature ignition behavior can be explained in terms of the alkylperoxy (RO_2) isomerization reactions that control the overall, low-temperature reaction rate. The RO_2 isomerization reactions with the highest rate constants have six membered transition states and generally occur between CH_2 groups. This type of RO_2 isomerization reaction also leads to a subsequent addition of O_2 followed by another isomerization and finally chain branching with the production of two OH radicals. It is this chain branching that contributes greatly to low temperature reactivity[5]. The CH_2 groups in HMN interact through six-membered ring RO_2 isomerization reactions that lead to a greater extent of chain-branching than seen for iso-octane which has only one CH_2 group.

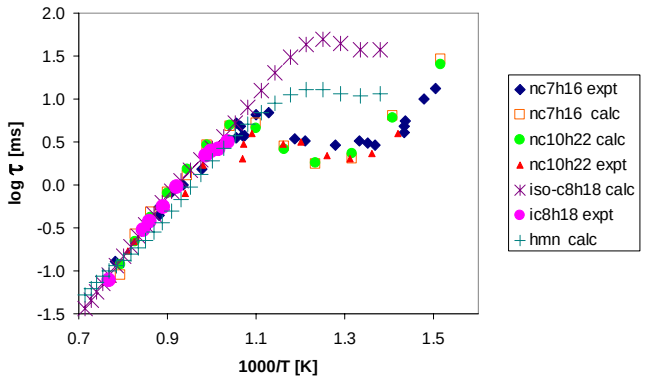

Figure 1 Autoignition of n-heptane, n-decane, iso-octane and 2,2,4,4,6,8,8-heptamethylnonane at 13 bar with stoichiometric, fuel/air mixtures. Computations: n-heptane (nc7h16)[6], iso-octane (ic8h18)[3], n-decane (nc10h22)[4], heptamethylnonane (hmn, present work). Experiments: n-heptane[7], iso- octane[8], n-decane[9]

Rate rules for hydrogen abstraction reactions. Electronic structure calculations at the CBS-QB3 level of theory combined with statistical mechanics and transition state theory have been used to calculate rate constants for the abstraction of H from primary, secondary and tertiary C-H bonds in alkanes by H atoms and CH_3 radicals, which are among the most abundant radicals in pyrolysis and combustion environments. Since the calculated rate constant for H abstraction by H atoms from methane agrees very well with the best literature data, we are confident that the applied methodology yields reliable rate constants for this reaction type. We found that all 15 individually calculated rate constants for primary C-H abstraction from linear and branched alkanes (C_2-C_6) by H atoms can easily be described by a single generic rate expression, if expressed on a per hydrogen basis. For temperatures above 500K the generic rate constant predicted the actual rate constant always to within 30%, in many cases significantly better. Similarly, the rate constants for 10 out of 11 investigated H abstraction reactions from secondary sites could be represented with similar accuracy by a single generic rate rule for this reaction family. Even the rate constant of the eleventh rate constant, which might be in error, deviates by less than 50% from the rate rule. Finally, we investigated 5 reactions involving H abstraction from tertiary C-H sites and the corresponding generic rate constant describes the individual rate constant to within 20% or better. Generic rate constants have also been derived for methyl radicals using the same set of reactants as above for H atoms. Again, each reaction family is well represented by a generic rate expression,

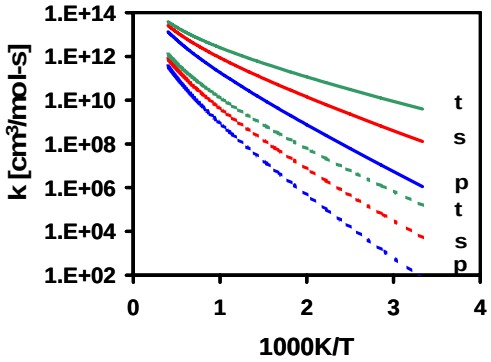

Figure 2 Rate rules for H abstraction per H atom from linear and branched alkanes by H atoms (upper 3 plots) and CH_3 radicals (lower 3 plots, broken lines). "p" , "s," "t" mark the plots corresponding to primary, secondary and tertiary C-H abstraction, respectively.

although larger deviations are observed. Nevertheless all representations are clearly within a factor of two, in most cases in the range of 10-40%. In Figure 2 the six generic rate constants are plotted against the inverse temperature. As expected, the abstraction rate constants increase from primary to tertiary C-H bonds and H abstraction reactions by CH_3 radicals are slower than those involving H atoms, not only because they have higher barriers but also smaller pre-exponential factors in the temperature region of interest.

Since we are interested in FT fuels, the question arises what impact the methyl substitution of alkanes will have on the initial radical pool formed via these abstraction reactions. Comparing, e.g., 2-methyl undecane with dodecane at a typical NTC temperature of 1100K, we notice (Table 1) several important points: (1) H abstraction by H and CH_3 leads to very comparable distributions, (2) Although only 1 of the 26 C-H bonds is tertiary, more than 10% of the radicals formed from H abstraction are predicted to be tertiary radicals. (3) Since substitution leads to more primary C-H bonds, the fraction of secondary radicals is significantly lower in 2-methyl undecane compared to dedecane. All predicted distributions reflect the initial radical composition. However, this distribution could significantly change if radical isomerization reactions are fast enough to compete with the radical consumption channels. Therefore kinetic mechanisms for FT fuels must also contain reliable rate expressions for isomerization reactions.

Table 1 Comparison of the initial radical distributions from H abstraction from 2-methyl undecane vs. dodecane by H and CH_3

Fuel	Abstraction by	Radical distribution at 1100K in %		
		Primary	Secondary	Tertiary
2-Methyl undecane	H	10.5	76.8	12.7
	CH_3	10.2	76.3	13.5
Dodecane	H	6.8	93.2	0.0
	CH_3	6.6	93.4	0.0

Rate rules for hydrogen shift reactions. The same computational approach as discussed above can also be used for intramolecular H abstraction reactions (H migrations). Since both reacting sites are from the same molecule, steric effects such as ring strain are expected to dominate the reactivity. This can be seen in Figure 3, which shows activation energies for a large number of isomerization reactions plotted against the heat of reaction. The data are clearly ordered with respect to the ring-size of the transition state: 3- or 4-membered transition states lead to high isomerization barriers in the range of 30-40 kcal/mol, while the barriers of transition states with 5-7 ring-members are significantly lower. For a given ring size, the barrier also depends on the heat of reaction (hence the types of C-H bonds that are broken and formed), and typical Evans-Polanyi relationships are observed. The ring-size of the transition state has also a dramatic impact on the A-factor. This can be seen from Table 2, which shows that the average A-factor decreases per frozen internal rotor by roughly 1 order of magnitude.

Table 2: Dependence of the A factor on the TS ring size

reaction	**1,2 shift**	**1,3 shift**	**1,4 shift**	**1,5 shift**	**1,6 shift**
TS ring size	**3**	**4**	**5**	**6**	**7**
# frozen rotors	**1**	**2**	**3**	**4**	**5**
A factor [s^{-1}]	**1.0E13**	**3.2E12**	**1.2E11**	**1.1E10**	**1.6E9**

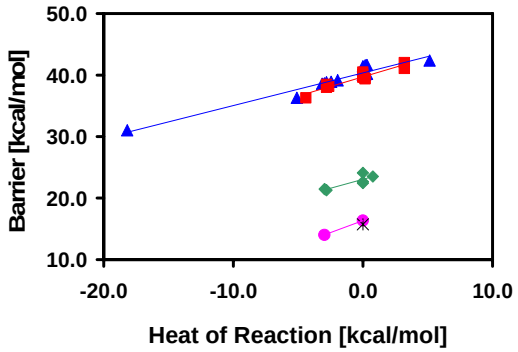

Figure 3 Activation energies for H migration in hydrocarbon radicals versus the heat of reaction. Blue triangle: 1,2-H shift, red squares: 1,3-H shift, green diamonds: 1,4-H shift, pink circles: 1,5 H shift and black star: 1,6 H shift.

Conclusions and next steps

The preliminary results presented here are just initial steps towards the goal to develop a surrogate model for FT diesel fuel, which then can be used to explore the difference between this fuel type and conventional diesel fuel. FT fuels generally contain iso-alkanes with one or two substituted methyl groups, and the combined model of n-alkanes, iso-octane and heptamethylnonane needs to be further expanded towards single and double substituted iso-alkanes. The discussed rate rules can help with some reactions, but additional rate rules covering β-scission reactions and abstractions by other radicals need to be generated or reevaluated. In addition, many reactions are pressure-dependent and fall-off behavior needs to be analyzed. Finally, our rate-rule discussion focused only on the pyrolysis chemistry aspect. Work is also in progress to improve our knowledge of the oxidation part of the mechanism.

Acknowledgements. This work at LLNL was supported by the U.S. Department of Energy, Office of Freedom CAR and Vehicle Technologies. The authors thank program managers Kevin Stork and Gurpreet Singh for their support. The LLNL work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. The work at CSM has been supported by the Office of Naval Research (N00014-05-1-0339, program manager Dr. Michele L. Anderson, and N00014-08-0539, program manager Dr. David Shiflcr), and by the National Renewable Energy Lab (NREL KXEA-3-33607-30, technical manager Mark Nimlos).

References

(1) Smith, B. L.; Bruno, T. J. *Journal of Propulsion and Power* **2008**, *24*, 618.
(2) Smith, B. L.; Bruno, T. J. *Industrial & Engineering Chemistry Research* **2007**, *46*, 310.
(3) Curran, H. J.; Gaffuri, P.; Pitz, W. J.; Westbrook, C. K. *Combustion and Flame* **2002**, *129*, 253.
(4) Westbrook, C. K.; Pitz, W. J.; Herbinet, O.; Curran, H. J.; Silke, E. J. *Combustion and Flame* **2008**, *in press*.
(5) Pitz, W. J.; Naik, C. V.; Mhaolduin, T. N.; Westbrook, C. K.; Curran, H. J.; Orme, J. P.; Simmie, J. M. *Proceedings of the Combustion Institute* **2007**, *31*, 267.
(6) Curran, H. J.; Gaffuri, P.; Pitz, W. J.; Westbrook, C. K. *Combustion and Flame* **1998**, *114*, 149.
(7) Ciezki, H. K.; Adomeit, G. *Combustion and Flame* **1993**, *93*, 421.
(8) Fieweger, K.; Blumenthal, R.; Adomeit, G. *Combustion and Flame* **1997**, *109*, 599.
(9) Pfahl, U.; Fieweger, K.; Adomeit, G. *Proceedings of the Combustion Institute* **1996**, *26*, 781.