Endothermic Fuels for Hypersonic Vehicles

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The use of hydrocarbon fuels for hypersonic vehicles will require increasing utilization of the fuel as vehicle speed increases. In order to achieve maximum heat sinks endothermic reactions must be employed to augment fuel enthalpy. Various reactions, such as thermal cracking, depolymerization, dehydrogenation, and dehydrocyclization, can be used and have been studied. Of these, the catalytic dehydrogenation of naphthenes shows the most promise for practical application. The dehydrogenation of MCH over a Pt/Al_2O_3 catalyst can approximately double the 1000 Btu/lb available from fuel enthalpy. This should provide cooling sufficient to allow flight into the range of Mach 10 at optimum altitude. However, the application of cooling to the various portions of the aircraft will present formidable problems. Factors that are important in this consideration such as thermal stability, reaction rate, reactor weight and volume, heat transfer, pressure drop, combustion characteristics, and the mating of the cooling system to the aircraft are discussed.

Nomenclature

a_k = constant in linear expression for heat capacity of species k
A_1, A_2 = kinetic constants, pre-exponential factors
A_f = wall effect factor in pressure drop equation
b_k = constant in linear expression for heat capacity of species k
B_1, B_2 = kinetic constants, temperature coefficients
Btu = British thermal units
C_p = heat capacity
C_{MCH} = concentration of methylcyclohexane
d_p = particle diameter
d_t = tube diameter
f = friction factor
G = mass velocity
g_c = gravitational conversion factor
ΔH = enthalpy change in reaction
h_p = heat-transfer coefficient, fluid-to-particle
h_w = heat-transfer coefficient, wall-to-packed bed
h = heat-transfer coefficient
k = noneddy part of effective radial thermal conductivity of packed bed
k_{eff} = effective thermal conductivity (radial) of packed bed
k_f = thermal conductivity of fluid
k_s = thermal conductivity of solid pellets of catalyst
k_w = thermal conductivity of tube wall
K_{eq} = equilibrium constant for reaction
L = reactor length
L/D = lift-drag ratio
LHSV = liquid hourly space velocity
m = wall thickness of reactor tube
MCH = methylcyclohexane
N_{Bi} = Biot number, $h_w r_t / k_{eff}$
N_{Nu} = Nusselt number, $h_w d_p / k_f$
N_{Pe} = Peclet number, $G d_p / D_r$ (where D_r is the radial diffusivity for mass) or $G_p G d_p / (k_{eff} - k)$
N_{Pr} = Prandtl number $C_p \mu_f / k_f$
N_{Re} = Reynolds number, $d_p G / \mu_f$
P = pressure
P_i = partial pressure of ith component
q/A = heat flux
Q = heat of reaction, $-\Delta H$
r = radius, position variable
r_t = tube radius
R = reaction rate
R_g = gas constant
S_h = source term in enthalpy equation
S_m = source term in material equation
T = temperature
T_0 = fluid temperature at reactor centerline
T_g = fluid temperature
T_w = temperature of inside wall of reactor tube
T_s = temperature of catalyst pellet
T_R = reference temperature
ΔT_w = temperature difference through metal tube wall
u = $(r/r_t)^2$, dimensionless radial variable
x = conversion
z = axial variable
ϵ = fraction
μ_f = viscosity of fluid
ρ = density of fluid
σ_r' = effective radiation constant
ω = coefficient in pressure drop equation for material and enthalpy transport
τ = ignition delay

Introduction

As airbreathing-engine-propelled vehicle speeds increase, thermal problems multiply because of the effect of stagnation temperature. While total cooling needs increase, the most critical regions are the leading edges and the engines. Although thermal effects can be somewhat accommodated by improved materials and passive cooling, sustained hypersonic flight in the atmosphere requires a substantial heat sink. Compared to a mechanical refrigeration system or a noncombustible coolant, the fuel is the best source of cooling.

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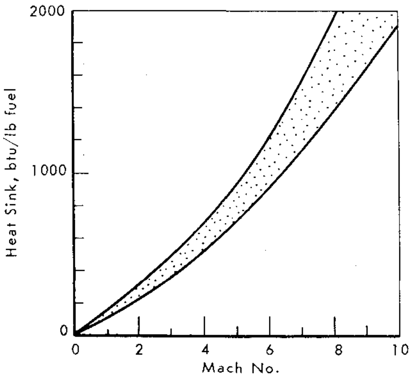


Fig. 1 Heat-sink requirement as a function of flight speed.

The speed limit on vehicles in the range above Mach 4 will depend on the cooling capacity the fuel can provide. Fuels such as liquid hydrogen, methane, and ammonia can contribute only sensible and latent heat, whereas certain hydrocarbon fuels can in addition provide cooling through endothermic reactions. Studies are now going forward to determine[1,2] how much cooling can be obtained in this way and how it can be utilized. Hydrocarbons can undergo both thermal (noncatalytic) and catalytic reactions. Theoretically, the total heat-sink capacities of hydrocarbon fuels range from about 50% to 112% of the cooling capacity of hydrogen (on a % heat of combustion basis) with laboratory proven capabilities up to about 85%. Thermal cracking is limited to about 55%, whereas catalytic reactions can achieve the higher figure (cf. Table 1).

Catalytic reactions of interest include dehydrogenation, dehydrocyclization, and depolymerization-type reactions. The most promising type that has been studied in the laboratory is the catalytic dehydrogenation of cyclic paraffins (naphthenes). This is typified by the dehydrogenation of methylcyclohexane over a platinum-on-alumina catalyst. Other promising reactions involve the catalytic dehydrogenation of dicyclohexyl and decahydronaphthalene.

Studies are also in progress on methods of application of cooling with hydrocarbon fuels. From the standpoint of the engine builder, the most straightforward procedure would involve a regenerative system. With packed catalyst beds, this may be difficult because of pressure drop, temperature, and heat-flux limitations. The possibilities of using intermittent beds, expanded catalyst supports, or dispersed catalyst systems (with a throwaway catalyst) are being studied. A more readily controllable but less efficient system of application would involve a secondary fluid cycle. An intermediate case would involve cooling a portion of the inlet air by heat exchange with the vaporizing and reacting fuel, the air being utilized thereafter for cooling by heat exchange, transpiration, or film techniques.

Improvements and testing of design features are being done both by analytical and by experimental methods. We have undertaken the determination of heat-transfer coefficients, improvement of catalytic activity and stability, development of improved catalyst systems, selection and testing of new fuel types, determination of fuel thermal stability, and determination of combustion properties of fuel and reaction products. The behavior of a fuel in a reacting system has been represented by a mathematical model. The properties of possible hydrocarbon fuels that could be used in hypersonic aircraft are being collected, correlated, and extended by means of both proprietary and literature correlations. This paper describes the methods being used, indicates the type of results being obtained, and attempts to pinpoint some of the critical areas of application.

Cooling Requirements

For every vehicle propelled by air-breathing engines there exists an altitude vs flight-speed corridor in which flight is feasible. The bounds of this corridor are set by the heat generated by stagnation effects during flight, the pressure in the engine, and the L/D of the aircraft. Roughly, one could say that the upper boundary of flight is set by lift, the lower, by drag and temperature. These factors can be modified by design such as the utilization of supersonic rather than subsonic combustion in the engine and of extensively swept wings of low cross-section area in the flight plane, and by proper selection of heat-resistant materials. Obviously, without specifying the entire aircraft and mission, it is impossible to determine precisely the amount of heat sink that will be required as a function of Mach number. However, a number of authors[3] have made educated guesses and these have been synthesized in Fig. 1, which gives the heat sink in terms of Btu/lb fuel burned as a function of Mach number, the indication being that about 2000 Btu/lb will be required at a speed of Mach 10. Flying at greater speeds obviously would require greater heat-sink capacity. Since most hydrocarbons can provide a maximum of only about 700–800 Btu/lb enthalpy on being heated from ambient to about 1000°F, it is obvious that flight speeds greater than about Mach 5 will require additional cooling capability. This region, generally known as the hypersonic region, is where endothermic reactions will have to be utilized in order to employ the higher hydrocarbon fuels successfully.

Heat-Sink Reactions

Thermal Reactions

The decomposition of hydrocarbons requires energy for its accomplishment, i.e., it is a possible heat-sink reaction. Such reactions have been investigated for application to hypersonic vehicle cooling by several investigators, including ourselves.[4,5] A number of reactions can be written that, if

Table 1 Endothermic capacities of some fuels

				Heat absorbed (1340°F, 10 atm.)				
				Btu/lb				
Fuel	Type reaction[a]	Products	Density, at 60°F, lb/ft^3	Chemical	Physical	Total	K, Btu/ cu ft	% of ΔH_c
Methane	None	...	18.7	...	1460	1460	41.6	6.8
Methylcyclohexane	Dh	C_7H_8, H_2	48.3	940	1016	1956	94.1	10.5
Dimethylcyclohexane	Dh	C_8H_8, H_2	49.6	785	1000	1785	88.5	9.6
Decalin	Dh	$C_{10}H_8$, H_2	56.0	950	1020	1970	110.3	10.8
SHELLDYNE-H[b]	Dh, TC	Mixed, H_2	67.5	(415)	(1000)	(1415)	(96)	(5.3)
JP-7[c]	TC	Mixed	49.5	310	860	1170	57.9	6.2
H_2	None	...	4.74	...	6500	6500	30.8	12.8

[a] Dh = dehydrogenation, TC = thermal cracking.
[b] Values in parentheses are estimated.
[c] Experimental, at 1200°F, 500–900 psi.

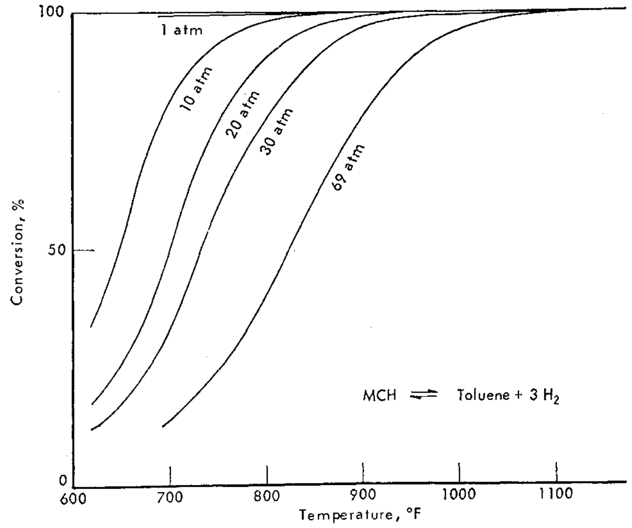


Fig. 2 Equilibrium conversion for the system methylcyclohexane-toluene-hydrogen.

they followed the course indicated, would supply substantial amounts of heat sink. Thus, the decomposition of propane into propylene and hydrogen would provide a heat sink of about 1200 Btu/lb: $C_3H_8 \rightarrow C_3H_6 + H_2$. However, the reaction does not follow this course. At 1400°F, propane reacts by means of complicated concurrent reactions that lead to the following over-all stoichiometric reaction:

$$C_3H_8 \rightarrow +0.05H_2 + 0.33CH_4 + 0.12C_2H_4 + 0.11C_2H_6 + 0.09C_3H_6 + 0.02C_4 + 0.01C_5H_{12} + 0.012C_6H_{14} + 0.36C_3H_8$$

The calculated heat sink of this reaction is 340 Btu/lb of propane; the measured value was about 300 Btu/lb. At higher conversions, the actual reaction is essentially thermally neutral due to increased formation of methane.

The following demonstrates several of the reaction routes available to propane, and the heat effects of the individual reactions:

$$C_3H_8 \rightarrow C_3H_6 + H_2,\ 1220\ \text{Btu/lb}$$
$$C_3H_8 \rightarrow C_2H_4 + CH_4,\ 770\ \text{Btu/lb}$$
$$2C_3H_8 \rightarrow 3C_2H_4 + 2H_2,\ 1240\ \text{Btu/lb}$$
$$2C_3H_8 \rightarrow 4CH_4 + 2C,\ -438\ \text{Btu/lb (exothermic)}$$

The effect of product distribution for the thermal decomposition of other hydrocarbons is shown in Table 2.

Catalytic Reactions

Catalysts have become increasingly important in industrial processing. A catalyst may serve either or both of two purposes: to increase the rate of a particular chemical reaction or to cause one of several possible reactions to occur selectively. In our case, we would want to increase the selectivity of the endothermic reaction. The concept of selectivity can be exemplified by referring to the uncatalyzed thermal reaction of propane in the previous section. In the absence of a catalyst the reaction proceeds at a certain temperature, yielding many products, some exothermic and others endothermic. A catalyst that would selectively enhance the rate of certain endothermic cracking or dehydrogenation reactions of propane to eliminate the formation of methane could increase the heat sink by as much as 300% over the thermal reaction.

Dehydrogenation reactions

The course of dehydrogenation of a hydrocarbon can be influenced by various catalysts leading more explicitly to desired products. The most practical way to do this, in this particular reaction, is to have the reaction go selectively to a product having a resonance-stabilized structure. This not only will produce a more reliable heat sink but also will influence the temperature regime of the thermodynamic equilibrium in favor of the desired products (Fig. 2). Thus, the reaction of cyclohexane

$$C_6H_{12} \xrightarrow{Pt/Al_2O_3} C_6H_6 + 3H_2$$

is endothermic by about 1250 Btu/lb and is thermodynamically favored because of the resonance stabilization of the benzene ring. We have investigated numerous other reactions of this type using Pt/Al_2O_3 as a catalyst. Thus, methylcyclohexane can be converted to toluene and hydrogen with a heat sink about 1000 Btu/lb. About the same heat sink can be obtained when decalin is converted to naphthalene and hydrogen and dicyclohexyl are converted to diphenyl and hydrogen. The ultimate fuel may be a blend of hydrocarbons in order to achieve optimization in such properties as freezing point, volatility, viscosity, lubricity, heat sink, thermal stability, etc. Addition of methyl groups to the basic ring structures can alter these properties, but the more methyl groups that are added the lower is the available heat sink.

Dehydrocyclization reactions

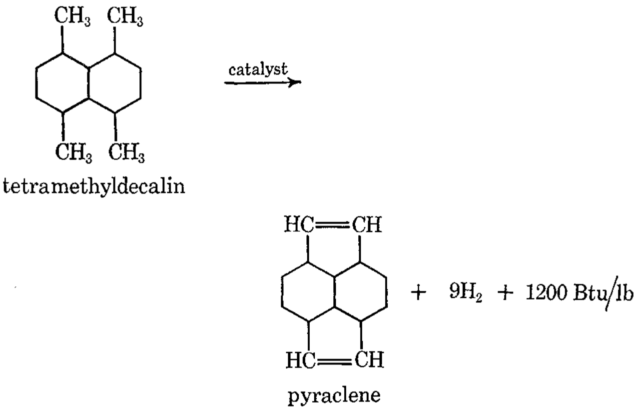
In principle, any hydrocarbon structure with sufficient carbon atoms in it could be cyclized to form C_5 or C_6 rings

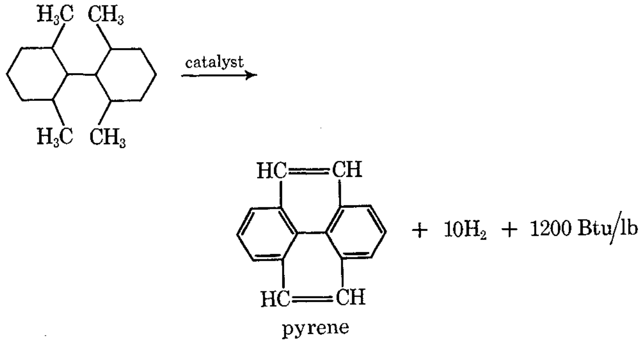
Table 2 Thermodynamic heats of reaction

Hydrocarbon	Reaction products	ΔH_R, Btu/lb
Methylcyclohexane	Toluene, H_2	940
	Benzene, H_2, CH_4	710
	Cyclohexene, CH_4	286
	Cracked products	-60^a
n-Octane	Octene, H_2	ca 900
	Octadiene, H_2	ca 900
	Styrene, H_2	1425
	Ethylbenzene (EB), H_2	957
	Xylene, H_2	915
	Toluene, H_2, CH_4	718
	Benzene, H_2, C_2H_6	804
	Cracked products	258
n-Dodecane	Dodecene	330
	Dodecadiene, H_2	595
	Aromatics, H_2	ca 640
	Cracked products	-110^a
n-Hexadecane (cetane)	Cracked products	131
Dicyclohexyl	Benzene, H_2	1038
	Toluene, pentane	325
	Cyclohexane (CH)	-94^a
	Hexane	-322^a
	MCH, pentane	-231^a
	Light gas	22
	Diphenyl, H_2	1080
	Phenylcyclohexane, H_2	540
Decalin	Naphthalene, H_2	950
	Tetralin, H_2	670
	CH + olefin	143
	MCH + olefin	143
	DMCH + olefin	143
	DECH	-110^a
	Benzene + olefin	800
	Toluene + olefin	800
	EB + olefin	800
	DEB	-700
	Alkyl aromatics	-400
Ethylbenzene	Styrene	509
	Toluene, CH_4	-273
	Benzene, C_2H_6	-180
	Benzene, C_2H_4	405
JP-7 (F-71), 1200°F	60% cracked, 50% gas	310^b

[a] Exothermic.
[b] Experimental.

and then dehydrogenated to give a high heat sink. Thus, normal octane could be cyclized to ethylcyclohexane and then dehydrogenated to styrene with a heat sink of about 1400 Btu/lb. However, the cyclization step, on any catalyst investigated so far, is relatively slow and not too selective, which means that the theoretical heat sink cannot be realized. It appears that the most promising utilization of this type of reaction will come in connection with already-formed cyclic structures. Thus, the addition of four methyl groups to decalin or dicyclohexyl in the proper places could improve the heat-sink capability of these structures:

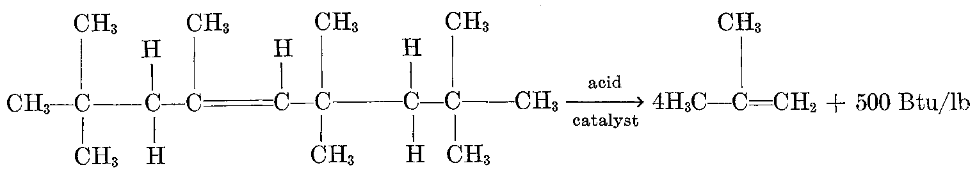




Here, the basic cyclic structure has been provided to direct the course of the reaction into the desired channel. However. the necessary catalysts to give the cyclization step sufficient selectivity have not been found, as yet.

Depolymerization

Since the chemical reaction of a polymerization is exothermic, it follows that the reverse reaction of depolymerization is endothermic. We have investigated, to some extent, the utility of this type of reaction to provide heat sink. For example,



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{C}=\overset{H}{C}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow[\text{catalyst}]{\text{acid}} 4H_3C-\overset{CH_3}{C}=CH_2 + 500\ \text{Btu/lb}$$

This reaction, in the presence of the proper catalyst, should occur rapidly and could be useful even though the heat sink is only 500 Btu/lb. This approach is potentially attractive for situations requiring only a limited heat sink, because of the ability of the petroleum industry to control the properties of the fuel by controlling the extent of polymerization in manufacture. However, because of the limited heat sink the necessary work to develop a satisfactory catalyst has not been undertaken.

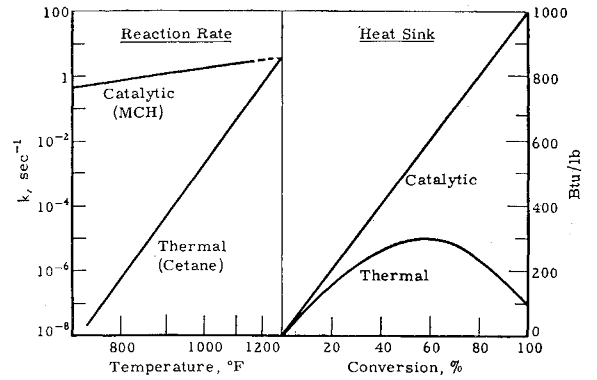


Fig. 3 Comparison of thermal and catalytic reactions.

Comparison of Thermal and Catalytic Reaction

The basis for favoring catalytic reactions rather than thermal is well illustrated in Fig. 3, which compares the thermal cracking of cetane and catalytic dehydrogenation of methylcyclohexane over a platinum-on-alumina catalyst. As shown on the right-hand side, the heat sink provided by the catalytic reaction is a direct function of the degree of conversion, since the selective reaction goes almost entirely to toluene and hydrogen. The greater the conversion, the greater the heat sink. The thermal reaction has a maximum heat sink of about 300 Btu's, which occurs at about 60 % conversion, and thereafter the heat sink actually decreases because this reaction is not selective and there are competing endothermic and exothermic reactions. Since, other things being equal, the extent of reaction depends on the thermal environment and the amount of heat being supplied, it is absolutely necessary that the reaction respond to a demand for cooling by providing a greater heat sink.

The left-hand side of Fig. 3 represents the response of the reactions to changes in temperature. Here, we see that the catalytic reaction has a high intrinsic rate and a low energy of activation and, hence, a high rate of reaction over a broad range of temperature. The thermal reaction, on the other hand, proceeds very slowly at low temperatures (such as 700°F), and although, because of the high energy of activation, it responds strongly to the effect of temperature, it does not reach comparable rates to the catalytic reaction until about 1200°F. This means that the catalytic reaction has a much broader range of temperature over which it can be used usefully for cooling. In addition, since the rate of reaction is primarily a function of the properties of the catalyst, it allows for the possibility of increasing the rate by devising better catalysts. This is not possible, of course, with thermal reactions.

Cooling Application Possibilities

There are various possibilities for engine design as a function of flight speed, which will affect the mode of application for cooling. It is possible that turbine engines would be used up to a speed of about Mach 4, a subsonic combustion ramjet at speeds up to about Mach 7, with a supersonic combustion ramjet being used at speeds above that (although the alternative of stretching the supersonic combustion ramjet operation down to the Mach 4 interface, as advocated by Ferri,[6] remains

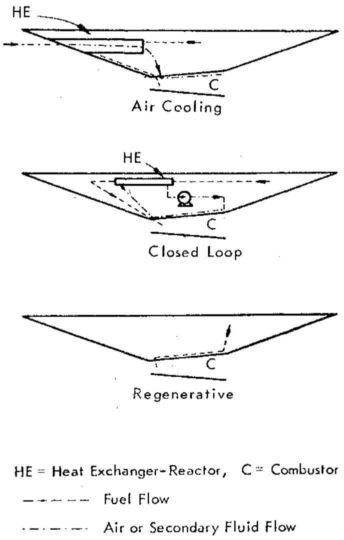


Fig. 4 Possible modes of application of cooling for hydrocarbon fuels.

an attractive possibility). The actual method of mating a cooling system to the engine, of course, remains to be determined and will be the end product of a considerable amount of work still to be done on the over-all project. However, in trying to determine the scope of the research that must be done to provide basic data for the project, three different ways of transferring the heat from the engine to the reactor exchanger have been considered. These are diagramed in Fig. 4, which represents ramjet engines traveling from right to left. They involve direct regenerative cooling between the combustion space and the fuel tubes (containing catalyst) forming the engine, a secondary loop design in which a circulating fluid is employed to transfer the heat from the engine to a reactor-exchanger containing the catalyst, and a system in which some of the inlet air (say 5–10%) is bled through a reactor-exchanger system and then employed to cool the walls of the engine by transpiration or film cooling. In this latter case, the reactor-exchanger might form the structural wall of the inlet system with a consequent saving in over-all structural engine weight.

We were concerned originally that excessive weight and volume penalties would have to be paid for the fact that, in order to get a reaction to go, a catalyst, which possesses both weight and bulk, must be provided. However, based on present results, it appears that these need not be large in proportion to the amount of fuel carried. Thus, in recent experiments on the dehydrogenation of methylcyclohexane (specific gravity = 0.78) over a platinum/alumina catalyst, a conversion of 85% was achieved at a LHSV of 625. In the referenced experiment, 25.1 lb/hr of MCH, equivalent to a flow rate of 60,000 lb/hr/ft^2, was passed through a 0.277-in. i.d. by 2-ft tube heated by direct resistance heating in a simulated fuel system. This means that with the type of catalyst used (Pt/Al$_2$O$_3$, $\frac{1}{16}$-in. pellets, specific gravity = 0.54) the amount of catalyst required would be 0.11% by weight of the amount of fuel consumed in one hour. This is, of course, trivial compared to the weight of the system required to contain the catalyst. It will be instructive to make an estimate of this weight. If we take the data from the same run and assume we have an actual MCH flow of 60,000 lb/hr/ft^2 for powering and cooling an engine, we find that the reactor volume would be 2 ft^3. If this is disposed in $\frac{3}{8}$-in. o.d. (0.277-in. i.d.) by 10-ft-long tubes, the number of tubes required would be 476 with a total outside area of 467 ft^2. Since operation is at high temperature and pressure, a fairly high wall thickness (0.049 in.) is assumed. Thus, the ratio of density of metal to that of packed catalyst is 18 and the weight of the tubes is 14.4 times the weight of catalyst they contain. For this particular example, the weight of the regenerative system then would be 1040 lb. However, this is not excessive if one considers that this could be part of the aircraft structure, presumably including sections of the combustion chamber, inlet system, and exhaust nozzle. For the secondary fluid system, the tubes must be mounted in an exchanger having provisions for contact with the secondary fluid on their exterior. Tubes may have to be finned on the outside to obtain satisfactory heat transfer from the secondary fluid. The secondary fluid circulation system and compressor must be provided. In accounting for these factors, we have assumed that such an arrangement can be provided with a volume only three times the volume of the catalyst and with a total weight only 1.5 times the weight of the catalyst and tubes (i.e., 23.1 times the weight of the catalyst). For this example, we calculate a weight of 1560 lb. The third method of transferring heat (and cooling capacity) between the engine and fuel, involving cooling a portion of the inlet air to the engine, has not been calculated, but presumably it would be intermediate between the requirements for the other two systems. The weights calculated, admittedly very roughly, do not seem excessive if we consider that the total weight of the fueled aircraft would be at least 100,000 lb/engine.

Mathematical Model

One of the objectives of our research program is to develop a mathematical model of the fuel system that can be integrated with a model for the combustion chamber and other heat-generating portions of the inlet and exhaust system of the vehicle as a function of flight speed, etc., to allow calculations to be carried out of the interaction between the fuel system and the operating conditions of the aircraft. In order to provide an experimental test of the mathematical model, we have constructed a well instrumented adiabatic fuel system simulation test rig (FSSTR), which, in its standard form, consists of three 10-ft sections of $\frac{3}{8}$-in.-o.d. by 0.049-in.-wall Hastelloy C tubing sections. Each tube is resistance heated by variable transformers, and up to 16 gal/hr of fuelcan be pumped through the system at 1000 lb/in.^{2}, gage. The standard arrangement can be varied by substituting other tube sections (e.g., $\frac{3}{4}$-in.-o.d. by 10 ft, and $\frac{3}{8}$-in.-o.d. by 2 ft).[7,8] An example of the type of data obtained is shown in Fig. 5.

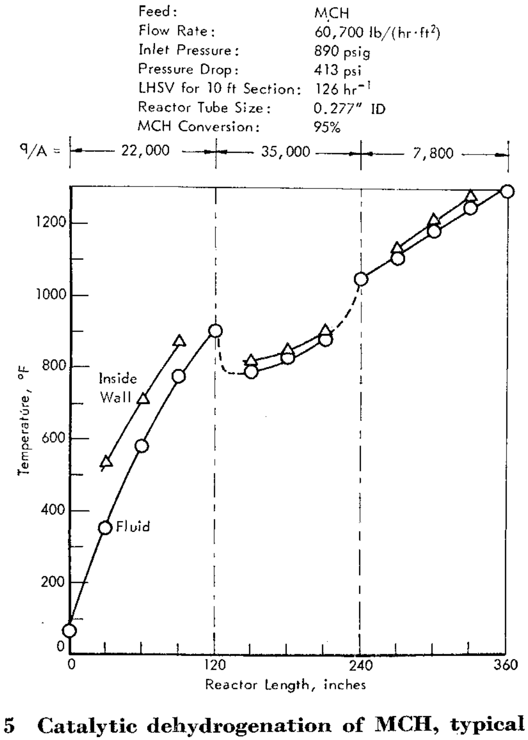


Fig. 5 Catalytic dehydrogenation of MCH, typical temperature profile, 10-ft reactor.

Results obtained in the FSSTR can be represented fairly well for open tubes by a Dittus-Boelter-type equation correlation, and for catalytic beds by a Hanratty-type equation, but these are essentially emperical correlations. In order to develop a more responsive continuum model, the procedure for a cylindrical packed bed reactor described in detail by Beek[9] was followed with the additional simplifying assumption that any radial variation in mass velocity of the fluid could be neglected. The basic assumptions made are then 1) the flow is axially symmetric and the mass velocity is uniform over the cross section, 2) axial diffusion and conduction may be neglected, and 3) molecular diffusion may be neglected. The last assumption is particularly important. By imposing the same (eddy) diffusivity on all chemical species, the material balance may be written in terms of conversion rather than concentration of each component.

With these assumptions the steady-state equations for material and energy transport are

$$\partial x/\partial z = (4d_p/r_t^2N_{Pe})[u(\partial^2 x/\partial u^2) + (\partial x/\partial u)] + R/G \quad (1)$$

and

$$\frac{\partial T}{\partial z} = \frac{4d_p}{r_t^2N_{Pe}}\left(u\frac{\partial^2 T}{\partial u^2} + \frac{\partial T}{\partial u}\right) + \frac{4k}{GC_pr_t^2}\left[u\frac{\partial^2 T}{\partial u^2} + \left(1 + \frac{u}{k}\frac{\partial k}{\partial u}\right)\frac{\partial T}{\partial u}\right] + \frac{4d_p}{r_t^2N_{Pe}} \times \left[2\left(\frac{\partial C_p}{\partial x}\right)\left(\frac{\partial x}{\partial u}\right) + \left(\frac{\partial C_p}{\partial T}\right)\left(\frac{\partial T}{\partial u}\right)\right]\frac{u}{C_p}\left(\frac{\partial T}{\partial u}\right) - \frac{RQ}{GC_p} \quad (2)$$

In both equations, the radial variable is expressed as $u = (r/r_t)^2$, which is the form used in subsequent numerical treatment of the equations. The material-transport equation employs the conversion, x, as the dependent variable. In writing the enthalpy-transport equation the radial diffusivity for heat is assumed to be the sum of an eddy diffusivity, contained in the Peclet number, and a noneddy diffusivity, k. Boundary conditions for temperature are set by standard equations.

It was possible on the basis of existing knowledge of processes in packed beds and of transport and thermodynamic properties of fluids to supply values for all the parameters appearing in the equations except those actually entering into the determination of the chemical reaction rate. The Peclet number was assumed to have a value of 10 for both mass and enthalpy transport. With the region of interest being clearly in the turbulent flow regime, the thermal conductivity was almost completely dominated by eddy conductivity except for the single empirical factor in the pressure drop expression and the expression relating to the rate of the chemical reaction to local concentrations and temperature. Thus, the model description of the packed bed reactor was constructed of correlations, parameter values, and assumptions available before any experiments were carried out.

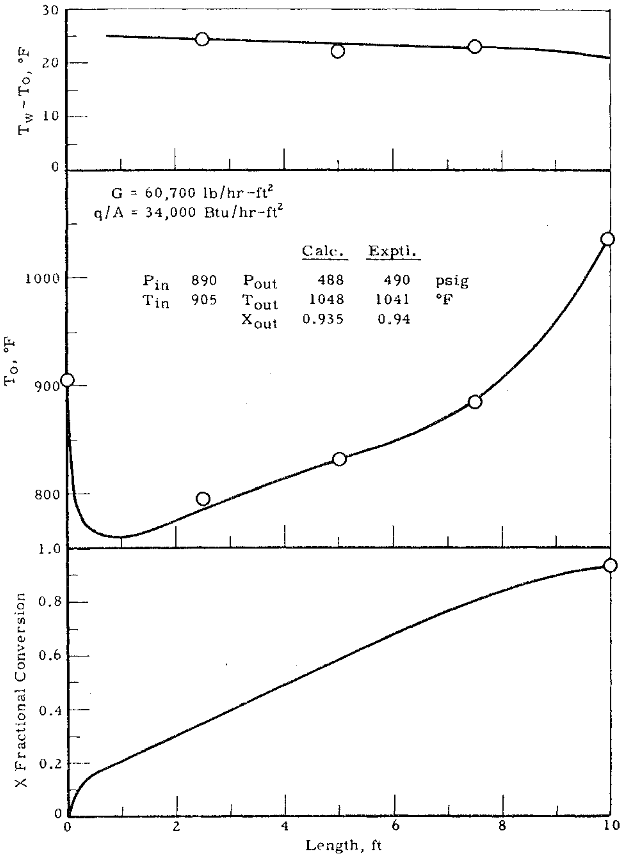


Fig. 6 Calculated axial profiles of conversion and temperature for MCH dehydrogenation, LHSV = 125, h = 1420.

Reaction kinetics turned out to be somewhat complex, varying between zero and first order for the dehydrogenation of methylcyclohexane. It was possible to use the kinetic form proposed by Sinfelt,[10,11] assuming Langmur-Hinshelwood kinetics in which the rate-determining step was the desorption of product. The value of R in Eq. (1) was then calculated in the following equation:

$$R = \frac{(1 - \epsilon)A_1C_{\text{MCH}} \exp B_1/R_gT_s}{1 + A_2C_{\text{MCH}} \exp B_2/R_gT_s}\left[1 - \frac{P_{\text{TOL}}\,P_{\text{H}_2}{}^3}{P_{\text{MCH}}K_{\text{eq}}}\right] \quad (3)$$

where the parameters had the values $A_1 = 100$ sec^{-1}, $A_2 = 2.8 \times 10^{-6}$ cc/g-mole, $B_1 = -3.0$ kcal/g-mole, and $B_2 = +30.0$ kcal/g-mole. In Eq. 3, the value on the right-hand side within the square bracket allowed for the reversibility of the reaction. The values of the parameters A_1, A_2, B_1, and B_2 could be determined by analysis of experiments carried out in laboratory reactors under isothermal conditions or by the results of a set of experiments in the FSSTR. The rate expression, when used in conjunction with the remainder of the packed reactor model, was required to reproduce not only the outlet temperature and conversion but also the axial profile of the temperature along the reactor centerline, which had been measured experimentally for each set of conditions (in the 10-ft tube). An example of the agreement between calculated and experimental values is given in Fig. 6 for an experiment in the 10-ft reactor-tube section. The agreement between the calculated wall temperatures and the measured values is better for the experiment represented in Fig. 6 than those represented by Fig. 7 for the 2-ft-long section. The experimental arrangements for the latter condition also were not as satisfactory because only the inlet and outlet fluid temperatures could be measured.

A higher heat flux was achieved in an experiment in which liquid methylcyclohexane was introduced into the 2-ft section at a flow rate of 153,200 lb/hr/ft² (LHSV = 1600). At a heat flux of 513,000 Btu/hr/ft², 44% conversion of MCH was achieved. In this experiment an average heat-transfer coefficient of 850 was observed, compared to about 1500 and 2100 under the other experimental conditions.

Combustion Characteristics

One of the early problems facing us with respect to the application of endothermic reactions to hydrocarbon fuels was the question as to whether the products of reaction would be suitable as a fuel for an engine. If the reaction involved dehydrogenation of a naphthene to an aromatic and hydrogen, there was no doubt as to the suitability of the hydrogen as a combustant, but aromatic hydrocarbons generally have been frowned upon as fuels for conventional continuous-combustion engines.

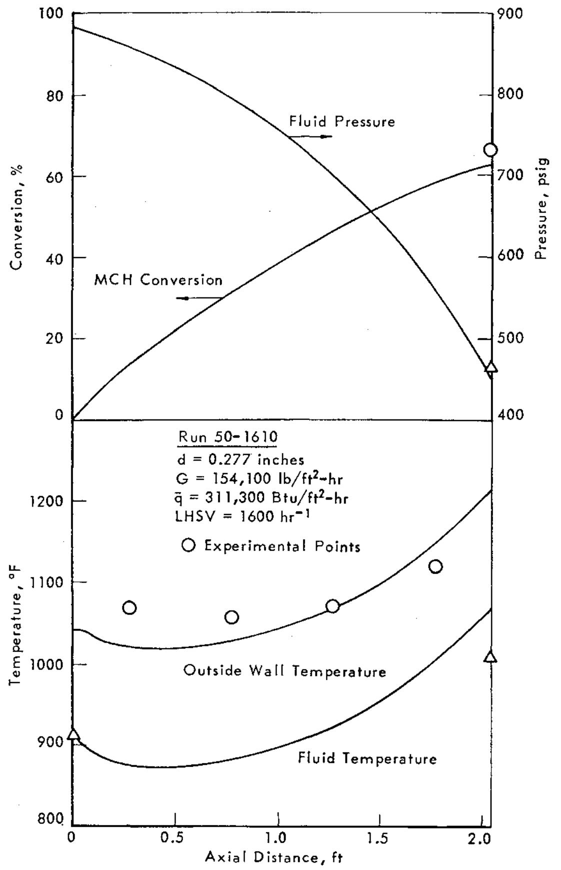


Fig. 7 Calculated profiles of P, T, and conversion for MCH dehydrogenation, $h = 2100$.

Subsonic Combustion

This was tested in a small laboratory burner under subsonic conditions. The combustion chamber itself was designed as a flexible piece of experimental equipment rather than as a small-scale simulation of a practical engine design. Primary factors of importance in the combustion of hydrocarbons in which we were interested were 1) the ability to burn the fuel with a low level of flame radiation (luminosity); 2) completeness of combustion in a reasonable combustor volume (combustion efficiency); 3) the absence or low level of carbon deposits in the combustor. Simulated products of reaction and unconverted feed were introduced into the combustor in vapor form at a temperature no lower than 450°F. Hot air was brought in tangentially through flow-directing vanes, and swirl mixing was allowed to take place in the inlet tube before the combustibles were brought into the combustion chamber. Combustion was observed, both visually and by means of an infrared detector, through sapphire windows located in three locations along the wall of the chamber, as well as through one axial window. A number of different fuel and reaction-product systems were burned in the burner, including propane, methylcyclohexane, toluene and hydrogen, toluene alone, decalin and methylnaphthalene, and methylnaphthalene and hydrogen. Axial pictures comparing propane, methylcyclohexane and toluene/3H_2 are shown in Fig. 8. All three fuels showed the same qualitative pattern of flame structure, size, and stability with change in equivalence ratio. Combustion-product samples were taken in some experiments. Under all conditions, sample combustion efficiency was found to be greater than 98.5%. When propane and toluene/3H_2 flames were viewed in a radiometer, the total radiation fluxes were 5000–7000 Btu/hr/ft^2 for propane and 6000–8000 for toluene/3H_2. The lowest fluxes were associated with the richest mixtures in both cases, presumably because of the lower flame temperature and lower production of the emitting species, CO_2 and H_2O. There was no indication of radiation from carbon particles with any fuel. We conclude that satisfactory combustion can be attained with toluene/3H_2 over the equivalence ratio range from 0.7 to 1.4.

Supersonic Combustion

Our approach to studying the supersonic combustion behavior of reaction mixtures produced by endothermic reactions was to determine the ignition delay in a shock tube over a range of temperatures and pressures equivalent to Mach numbers from 2 to 4. The details of the early part of the study have been given in a previous paper.[12] Our instrument is a single-diaphragm, 3-in.^{2}, aluminum shock tube instrumented to detect the arrival of the shock by means of the pressure generated and to observe the ignition delay by either visual or infrared emission resulting from combustion. A large number of experiments have been done with different hydrocarbon species, and the essence of the results is displayed in Fig. 9, in which the ignition delay is plotted as a function of the reciprocal of the absolute temperature at a particular equivalence ratio, pressure, and diluent concentration. General conclusions to be drawn from these studies are that for C_3 and higher hydrocarbons, no great dependence of ignition delay on molecular weight or molecular structure is evident, although, generally, straight-chain paraffins have somewhat shorter delays than the branched or cyclic structures, and aromatics have longer delays than corresponding naphthenes. However, the im-

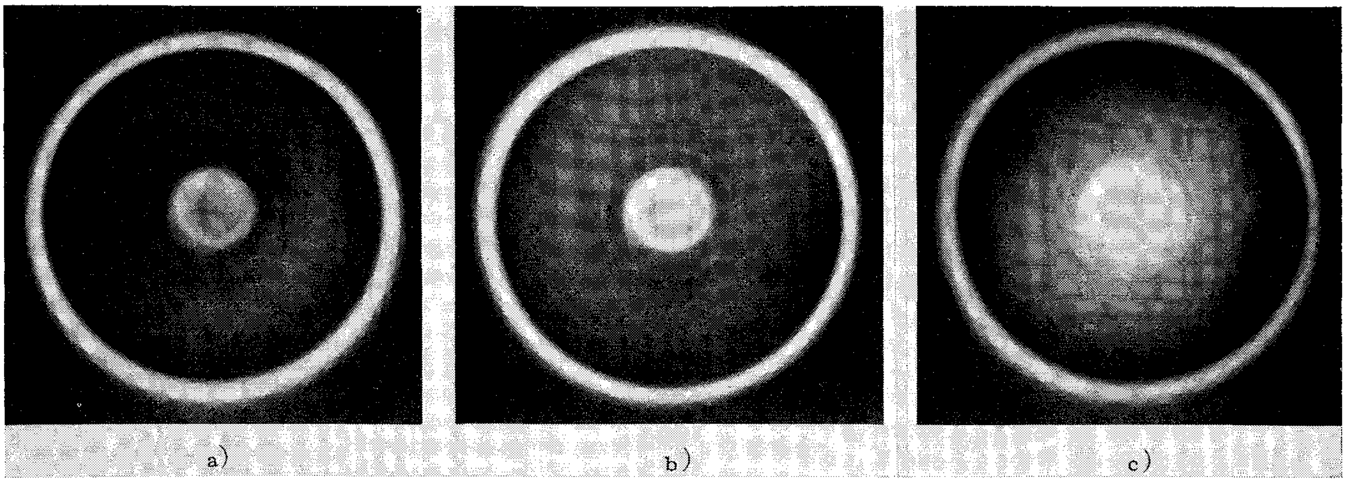


Fig. 8 Photographs of stoichiometric flames; 5 lb/hr fuel, 1.0 atm, fuel: a) propane, b) MCH, and c) toluene/3H_2.

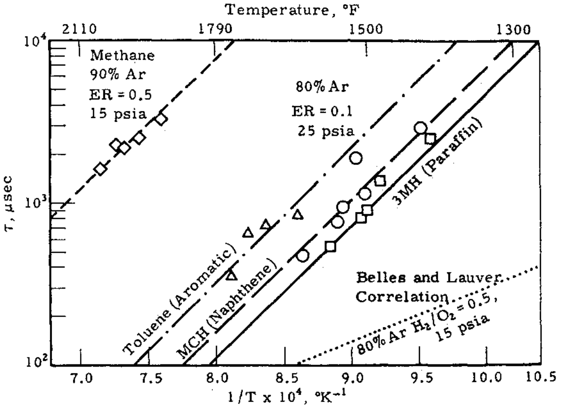


Fig. 9 Ignition delay as a function of temperature for hydrocarbons and H_2.

portant conclusion with respect to the present application is that a mixture of an aromatic with its attendant hydrogen formed by reaction gives very closely the same ignition delay as the parent cyclic hydrocarbon from which it was generated. It will be noted that the first member of the hydrocarbon paraffin series, methane, has a very much longer ignition delay than the higher members. This singularity is due to the fact that the initial response of a hydrocarbon to the energy transmitted to it by a shock is generally to undergo dehydrogenation, producing hydrogen atoms that are the species probably responsible for initiating the ignition reaction.[13] This is most difficult with methane, because of the high bond strength of primary C—H bonds. Also, it is noted that even the higher hydrocarbons have much longer delays than hydrogen at low temperatures. Owing to the high energies of activation for ignition for hydrocarbons compared to hydrogen (35 vs 10 kcal), the ignition delays of hydrocarbons shorten more rapidly as the temperature is increased. Values merge at temperatures somewhat in excess of 1800°F, becoming less than 100 µsec for both systems. However, the longer ignition delays of hydrocarbons at lower temperatures are undoubtedly responsible for the difficulties which have been observed experimentally in the self-piloting of hydrocarbon flames under supersonic combustion conditions.

Conclusions

1) The application of the endothermic reaction principle appears to be possible with hydrocarbon fuels, providing catalytic reactions are utilized for bringing about the desired reaction. 2) Fuels such as methylcyclohexane, decalin, and dicyclohexyl appear to have the capability of providing cooling for vehicles utilizing hydrocarbon fuels up to the range of about Mach 9 or 10. 3) Considerable improvement in the presently contemplated mode of application of hydrocarbon cooling appears to be possible, and may be necessary before satisfactory technical application can be achieved. 4) Our understanding of the dehydrogenation of methylcyclohexane appears to be in a sufficiently advanced state to warrant the recommendation that flight testing in a ramjet engine, to be attached to a vehicle such as X-15, should be contemplated in the near future.

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