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Initiators for Endothermic Fuels

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Aircraft designed for hypersonic flight must incorporate active cooling in the propulsion system. Hydrocarbon cracking reactions produce a high endotherm; however, without a catalyst these reactions require very high temperatures, which reduces the allowable stress in the heat exchanger materials and increases wall thickness and weight. The goal of this investigation was to determine if chemical initiators could accelerate the rate of hydrocarbon cracking reactions and reduce the required temperatures in a hypersonic aircraft heat exchanger/reactor. We mixed numerous initiators with *n*-heptane and measured the rate of cracking. These tests were conducted at temperatures of 450, 500, and 550°C, and at a pressure of 37 atm. We identified several chemicals that produced substantial increases in measured cracking rates when added to the fuel at concentrations from 0.5 to 2.0 wt%. The best initiator is soluble in the fuel, stable in its concentrated form, and is not highly toxic.

Introduction

AIRCRAFT designed for hypersonic flight must incorporate active cooling in the propulsion system. At low Mach numbers the heat loads are low, and sensible heating of the fuel can provide sufficient heat sink. At high Mach numbers heat loads exceed those available from sensible heating of the fuel. Therefore, endothermic reactions are needed to augment the cooling capacity of the fuel.

One example of an endothermic reaction is the dehydrogenation of methylcyclohexane to toluene and hydrogen as shown here:

$$C_7H_{14} \rightarrow C_7H_8 + 3H_2 \tag{1}$$

This reaction, which has a chemical endotherm of 940 Btu/lb, was identified as a potential source of cooling in earlier investigations of endothermic fuels.[1,2] However, a catalyst is required for this reaction to occur at a rate that will produce the necessary cooling. Catalysts composed of platinum supported on high surface area alumina have been shown to work well in this application.[1,2]

The use of a solid catalyst complicates the design and construction of a heat exchanger/reactor. Because the thermal conductivity of a catalyst is very low, the catalyst must be applied in very thin layers (5–100 μm) to metal heat-transfer surfaces to maximize heat flux. However, regardless of the thickness, the presence of the catalyst layer represents a barrier to heat transfer. Therefore, the maximum heat flux achievable with a catalyst present will always be lower than without the catalyst. To compensate for the reduced heat flux, the size and weight of a heat exchanger/reactor that incorporates a solid catalyst will always be larger than a heat exchanger/reactor that does not. In addition, attachment of the catalyst layers to heat-transfer surfaces in narrow flow passages is difficult. Reactor designs must accommodate the need for access to the fuel side heat-transfer surfaces. This adds to the size, complexity, and cost of the heat exchanger/reactor. Another problem with solid catalysts is a limited lifetime. Catalysts can fail by either deactivation or disbonding from the metal surface. If a catalyst is used, periodic regeneration of the catalyst, either by in situ regeneration or by replacement, is likely to be required.

Another potentially useful endothermic reaction for hypersonic aircraft is normal paraffin cracking. Cracking reactions, which convert high molecular weight paraffins into mixtures of lighter olefins and paraffins, can be conducted either with or without solid catalysts. Catalytic cracking is carried out at relatively low temperatures, 400–550°C, in the presence of acidic compounds such as zeolites.[3] Thermal cracking, on the other hand, is a gas phase reaction and requires higher temperatures, above 500°C, for the reaction to occur at useful rates.

Although catalytic cracking and thermal cracking reactions both produce a mixture of low molecular weight hydrocarbons; they occur by different mechanisms and result in different product distributions.[3] The catalytic mechanism occurs by way of carbenium ion intermediates on the catalyst surface and produces high concentrations of C_3 and C_4 products and very few C_1 and C_2 products. On the other hand, the thermal cracking reaction occurs by a free radical mechanism and results in high concentrations of C_2 and C_3 compounds.

In addition to the problems of incorporating a solid catalyst in a heat exchanger as just described, cracking catalysts typically deactivate rapidly (within seconds at ambient pressures) by accumulation of coke.[3,4] This problem has a significant impact on the operation of industrial catalytic cracking units that use zeolite catalysts to process about 35% of the crude oil consumed in the U.S. every year.[5] To accommodate this rapid deactivation, the process is carried out in fluidized bed reactors that continually cycle the catalyst between the fuel and a regeneration unit, where coke is removed by oxidation at high temperatures.

Catalytic cracking under supercritical conditions (where endothermic fuels systems would operate) also does not appear to be well suited for cooling hypersonic aircraft. In a study of *n*-heptane cracking over zeolite catalysts at pressures of 38 atm and at temperature of 475°C, the carbon-based selectivity for coke increased from 25% at startup to about 40% after 200 min on stream.[4] Although the supercritical fluid apparently helps remove coke by dissolution, the catalyst still exhibited substantial deactivation in the first few minutes of testing. In addition this work shows that cracking at supercritical pressures reduces the overall concentration of olefins in the products, which reduces the endotherm of the reaction. Results show that after about 25 min on stream, the propane-to-propylene ratio in the products is about 2.5 when the reaction pressure is about 4.6 atm (subcritical pressure). On the other hand, the ratio is about 5.0 when the reaction is conducted at supercritical pressures (38 atm). Thus, we conclude that, even at supercritical conditions, zeolite catalysts deactivate rapidly and exhibit high selectivity for coke and low selectivity for olefins. These results suggest that catalytic cracking would not be a suitable reaction for use onboard a hypersonic vehicle.

Thermal cracking, on the other hand, does not require a catalyst and also has better selectivity for olefins. Therefore, this reaction appears to be an attractive candidate for achieving high endotherms. However, thermal cracking reactions currently are difficult to use because they require very high temperatures in order to achieve

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useful reaction rates. These extreme temperatures reduce the allowable stress in the heat-exchanger materials requiring increased wall thickness to avoid mechanical failure. In addition, because the efficiency of the heat exchanger decreases as the operating temperature increases, the size of the heat exchanger increases with temperature. The result is that small increases or reductions in the operating temperature translate into significant increases or decreases in the heat-exchanger design weight.

However, if the rate of thermal cracking could be accelerated at lower temperatures by addition of a fuel additive, then this reaction would become a very attractive candidate for use in an endothermic fuel system. The purpose of this investigation was to determine if fuel additives could be developed that would allow thermal cracking to occur at lower temperatures. In the following sections we discuss the thermal cracking mechanism and then illustrate how a fuel additive could accelerate the rate of cracking.

Thermal Cracking Mechanisms

Thermal cracking of aliphatic hydrocarbons, such as *n*-heptane, is a noncatalytic process that can produce high yields of alkenes resulting in a highly endothermic reaction. An example of such a cracking reaction is shown in Eq. (2). Here, *n*-heptane reacts to form three moles of ethylene and one mole of methane; the enthalpy of this reaction is +62.8 kcal/mole.[6]

$$C_7H_{16} \rightarrow 3C_2H_4 + CH_4 \tag{2}$$

Although we have shown Eq. (2) as a single-step reaction, it actually occurs in a series of steps involving a chain reaction mechanism. The reaction is initiated by heating the heptane to high temperatures in the absence of a catalyst. This causes the homolytic cleavage of a C−H or a C−C bond within the molecule. The reaction leaves two fragments, each containing an unpaired electron or a free radical. An example of such an initiation step is shown next:

$$C_7H_{16} \rightarrow C_7H_{15}\cdot + H\cdot \tag{3}$$

For simplicity, we have only shown the cleavage of a single C−H bond; in practice, several different C−C and C−H bonds would break, leading to a mixture of products. However, this case illustrates the basic concept of the thermal cracking reaction.

The C_7 free radical segment formed in Eq. (3) is a relatively reactive species and undergoes a decomposition process that produces ethylene and a primary radical with two less carbons. The formation of ethylene is the outcome of a process called β-scission.[3] In this step the second bond from the radical carbon is homolytically cleaved, leaving the primary radical and an ethylene molecule. The β-scission step is shown in Eq. (4):

$$C_7H_{15}\cdot \rightarrow C_5H_{11}\cdot + C_2H_4 \tag{4}$$

The radical formed in Eq. (4) can continue to undergo β-scission, each time producing a molecule of ethylene until ultimately a methyl radical is formed. The methyl radical then abstracts a hydrogen radical from a neighboring molecule. If the reaction is not close to completion, the most likely candidate for the methyl radical to react with is another *n*-heptane molecule. This step results in the production of an additional hydrocarbon radical along with methane as shown next:

$$C_7H_{16} + CH_3\cdot \rightarrow C_7H_{15}\cdot + CH_4 \tag{5}$$

Continuous repetition of the reactions shown in Eqs. (4) and (5) leads to the formation of 75% ethylene and 25% methane. This sequence also shows that once a free radical is formed it can initiate the decomposition of an unlimited number of hydrocarbon molecules.

For simplicity, we have limited the discussion to a reaction scheme where the radical first forms on the terminal carbon in the *n*-heptane molecule, resulting in the production of ethylene and methane. In practice, the radical can form on any of the carbon atoms, producing a mixture of lighter alkanes and alkenes.

As the conversion increases and the concentration of *n*-heptane decreases, the chances of the methyl radical reacting with another heptane molecule decrease, and at the same time the probability of two methyl radicals recombining increases. This is the termination phase of the reaction:

$$2CH_3\cdot \rightarrow C_2H_6 \tag{6}$$

Although we only have shown the recombination of the methyl radicals, recombination between any two radicals could also occur. These reactions occur at the end of the sequence after the majority of products have been formed. These products thus account for only a very small portion of the product distribution and are usually ignored in the overall mass and energy balance of the reaction.

Use of an Initiator to Accelerate Thermal Cracking Reactions

In a chain reaction such as that just described, the overall reaction rate is determined by the rate of the slowest step in the sequence. In this sequence the slowest step is free radical generation [Eq. (3)]. Therefore, addition of a chemical that produces more free radicals can result in an increase in the overall rate of thermal cracking reaction. Such a chemical would be one that has bonds that are weaker than the C−H or C−C bonds in the *n*-heptane molecule. This compound is a chemical initiator.

If an initiator is added to the fuel, the reaction sequence is slightly different than the one just shown. The first step in the sequence is the homolytic cleavage of the bond within the initiator molecule to form initiator radicals:

$$A{-}A \rightarrow 2A\cdot \tag{7}$$

Because the A−A bond broken in this step is somewhat weaker than the C−C or C−H bonds in the fuel molecule, this reaction proceeds much more rapidly than that shown in Eq. (3). Once formed, the initiator radicals then abstract a hydrogen radical from a *n*-heptane molecule to produce the hydrocarbon radical and an AH molecule:

$$C_7H_{16} + A\cdot \rightarrow C_7H_{15}\cdot + AH \tag{8}$$

At this point the reaction path becomes similar to the path described without the initiator. The hydrocarbon radical undergoes a series of β-scission steps producing ethylene molecules and ultimately a methyl radical, which then reacts with a heptane molecule to form another radical. As was the case for the reaction without the initiator, the continued repetition of Eqs. (4) and (5) results in the formation of ethylene and methane.

Again, the overall reaction even in the presence of an initiator is described by Eq. (2). The initiator is not a true reactant; its only function is to start the cracking reaction. As a result, it can be effective in very small quantities.

For an initiator to be effective, the active bond (the one that undergoes homolytic cleavage in the initiation reaction) must be somewhat weaker than those contained in the fuel molecule. Currently, the most common use of initiators is in the initiation of polymerization reactions, which occur at relatively low temperatures and pressures. Examples of compounds that have been used in these applications include azo compounds (R−N=N−R) and peroxides (R−O−O−R).[7] The active bond strengths found in these compounds range between 30 and 60 kcal/mole. By comparison, the energy required to break a C−H or C−C bond is much greater, over 80 kcal/mole.

The successful development of an initiator would have several advantages over relying on purely thermal cracking to achieve the desired cooling. First, the temperature at which a given cracking rate occurs could be decreased by as much as 100°C. Second, the additional cooling capability could be accessed only when desired. A schematic of how such a system would be employed is shown in Fig. 1. This figure shows that the injection of the initiator upstream from the heat exchanger is accomplished by a metering pump, which uses a temperature feedback loop from a point downstream of the heat exchanger for control. Here the initiator pump is only activated when the control temperature exceeds a preset value. When

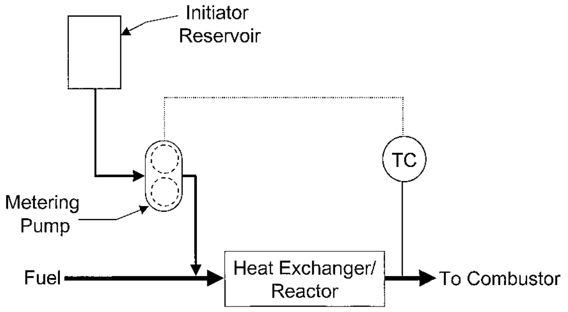

Fig. 1 Schematic of an onboard system for the injection of a chemical initiator.

the temperature is reduced, the initiator flow is reduced or stopped completely. The installation of the hardware required to store and deliver the initiator into the fuel represents the primary disadvantage associated with the use of a chemical initiator.

Experimental Methods

The goal of the experimental program was to test the effectiveness of different potential initiator compounds in order to determine the effectiveness of each in accelerating the rate of alkane cracking. Because commercial initiators were not designed for this reaction, there are relatively little data available discussing the use of initiators in this application. We thus were required to carry out laboratory tests simulating expected reaction conditions to test the effectiveness of potential initiators. The apparatus we used to test candidate initiators consists of three primary sections: a manifold for introduction of fuel and initiator at high pressures, a heated reactor section where the cracking reaction occurs, and the analytical equipment required to measure the extent of the cracking reactions. The *n*-heptane feed was introduced into the intake manifold and reaction chamber by a high-pressure liquid pump (ISCO 5000) that can maintain reaction pressures of over 68 atm. We used a second high-pressure liquid pump (Waters 510) to introduce the initiator solution into feed stream prior to the reactor. Reaction pressure was maintained by a pressure control valve downstream of the test section with the pressure feedback coming from a pressure transducer located in the fuel line upstream from the preheater.

There are two advantages to adding the initiator to the feed stream through a separate line rather than mixing the initiator with fuel and then adding both through the existing single line. First, we were able to establish steady-state conditions with fuel only and then measure the change in reaction rate caused by adding the initiator. The second advantage is that we were able to vary the initiator concentration during a run by changing the flow rates of both pumps.

The reactor test section consisted of a 0.635-cm o.d. × 0.318-cm i.d. stainless-steel tube, which was lined with copper to prevent filamentous coke formation. The reactor length was 30.5 cm, resulting in a volume of 0.5 cm. The test section was enclosed by a Lindberg tube furnace, which was capable of heating the reactor test section in excess of 600°C. We used a thermocouple inserted into the flowpath at the exit of the test section to provide feedback for the power output to the tube furnace.

We initially carried out reactions using test sections made of stainless steel or nickel and found that the reactor rapidly was plugged when the reactor temperature was 550°C or higher. Examination of the carbon deposits indicated that the material consisted primarily of filaments of carbon. The formation of carbon filaments when fuel is exposed to metals such as iron or nickel has been well documented and can be a serious problem in heat exchangers where hot fuel comes into contact with metal surfaces.[8,9] We then carried out tests to identify coatings, which could be applied to the inner surface of the test section and found that lining the inside of the test section with copper prevented filamentous coke. Copper does not form a metal carbide and therefore eliminates the first step in the coke formation process.[9] The use of copper-lined tubes allowed us to operate for long periods of time without plugging the reactor section.

We passed a small portion of the stream exiting the reactor through two SRI Model 8610 gas chromatographs (GC) for analysis of the products. One GC contained a 1-m × 0.318-cm column packed with silica gel and a thermal conductivity detector. This GC was used to measure the concentrations of cracked products along with unreacted fuel. The second GC contained a 3.3-m × 0.318-cm column packed with 5% Bentone 34, 5% SP1200 on Suppelcoport, and a flame ionization detector. This GC was used to measure the concentration of unreacted initiator in the stream exiting the reactor.

We carried out experiments at a fuel flow rate of 325 cc fuel/cc reactor per hour (or liquid hourly space velocity = 325 h^{-1}). We first measured the percent fuel cracked at 450°C (bulk temperature at the exit of the test section) with no initiator present. We then added 0.5 wt% initiator and obtained GC measurements to determine the effect that the initiator had on the amount of fuel cracked. We also measured the cracking levels with initiator concentrations of 1.0 and 2.0 wt%, obtaining at least two GC measurements at each initiator concentration. We then stopped the initiator flow and repeated the background measurements resulting from purely thermal cracking at 450°C. We repeated this sequence 500 and 550°C. By measuring the background or thermal cracking rate obtained at each temperature and then measuring the rate with different concentrations of initiator, we obtained a direct measure of the effect of the initiator on the cracking rate. This procedure eliminates ambiguity that can result from comparing the results of different experiments caused by small changes in temperatures, pressures, or flow rates.

Results and Discussion

We carried out several series of tests in our experimental program. One series was performed in which we tested many different candidate initiators in order to determine their effect on a normal alkane model fuel, *n*-heptane. We also carried out tests to determine the effectiveness of the initiator on a model isoparaffin, 2,2,4-trimethylpentane (or isooctane).

Results of Initiator Tests Using *n*-heptane Fuel

We first carried out tests in which the effects of candidate initiators were measured using *n*-heptane fuel. The initiators tested were compounds composed primarily of carbon and hydrogen and which also contained smaller quantities of either oxygen and or nitrogen. These compounds included many of the commercially available initiators such as 2,2-azobisisobutyroritrile (AIBN). Although some of the commercial initiators showed moderate effectiveness, they required significant quantities of solvents such as acetone to achieve desired solubility, and they are unstable in their concentrated form. We then tested other compounds that have not been identified as free radical initiators and identified several compounds that were much more effective than the commercially available initiators. In addition, these compounds are soluble in the fuel being tested, they are stable in their concentrated form, and they are not highly toxic. We believe that the use of compounds which are soluble in fuel and do not present unusual hazards when handled would result in a system that could be more easily installed on a high Mach aircraft.

Figure 2 shows the cracking rates we measured for the most active initiator we have identified to date. This figure shows *n*-heptane cracking rates measured at 450, 500, and 550°C with initiator concentrations of 0, 0.5, 1.0, and 2.0 wt%. This figure shows that at these reaction temperatures adding initiator to the fuel significantly increases the rate of *n*-heptane cracking. We see that at 450°C the rate of cracking without initiator is 0.018 mole heptane/h cc, which is close to our limit of detection. However, when we add initiator, we see that the reaction rate has increased to 0.20 moles/h cc, almost a factor of 10 improvement in reaction rate. We also see that at this temperature the reaction rates do not vary strongly with initiator concentrations above 0.5 wt%. At 500°C Fig. 2 shows that the thermal cracking (without initiator) rate is 0.080 moles/h cc and that the presence of initiator again results in a substantial improvement in rate. Addition of 0.5 wt% initiator results in a value of 0.43 moles/h cc, whereas addition of 2.0 wt% initiator results in a rate of 0.51 moles/h cc. Figure 2 shows that similar results are obtained at 550°C. Addition of 0.5 wt% initiator results in an

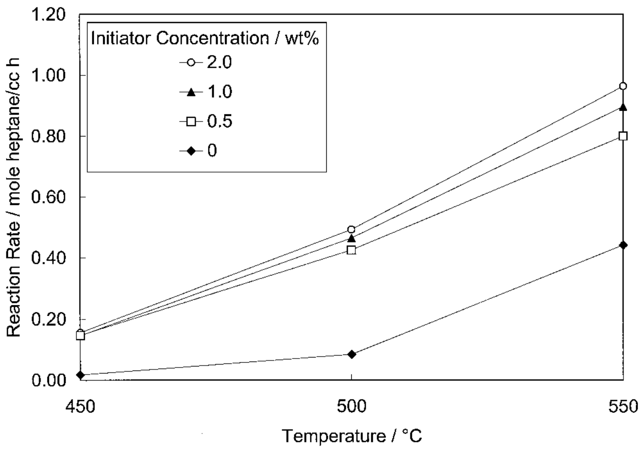

Fig. 2 Cracking rates obtained for *n*-heptane with up to 2.0 wt% initiator added.

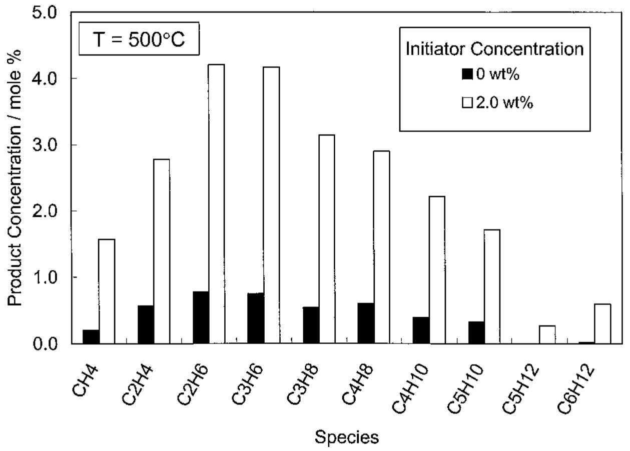

Fig. 3 Product distribution from *n*-heptane cracking at 500°C with and without initiator.

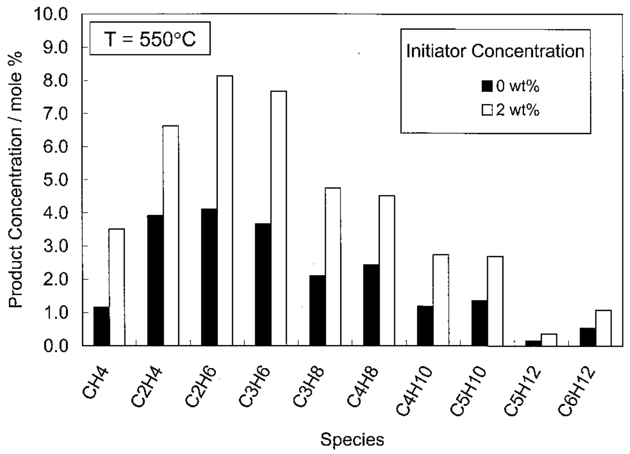

Fig. 4 Product distribution from *n*-heptane cracking at 550°C with and without initiator.

improvement in rate from 0.44 to 0.81 moles/h cc. Increasing the initiator concentration to 2.0 wt% results in a rate of 0.97 moles/h cc. Overall, the data presented in Fig. 2 clearly demonstrate that the addition of initiator produces substantial increases in the rate of *n*-heptane cracking.

In our discussion of the effects of initiator, we suggested that the initiator should only accelerate the cracking rate and should not alter the reaction mechanism. If this is true, we should not see any significant difference in product distribution between initiated and noninitiated cracking. In Figs. 3 and 4 we compare the product distribution obtained with and without initiator at reaction temperatures of 500 and 550°C, respectively. (Because the concentrations of products at 450°C without initiator were very low, we did not include a comparison at this temperature). We see that at reaction temperatures of 500 and 550°C, when no initiator is present, the product distribution is centered around the C_2 and C_3 alkanes and alkenes. This type of product distribution, particularly the presence of the C_2 species, is consistent with that expected from thermal cracking and is consistent with measured product distributions obtained from the thermal cracking of other normal alkanes at supercritical pressures.[10]

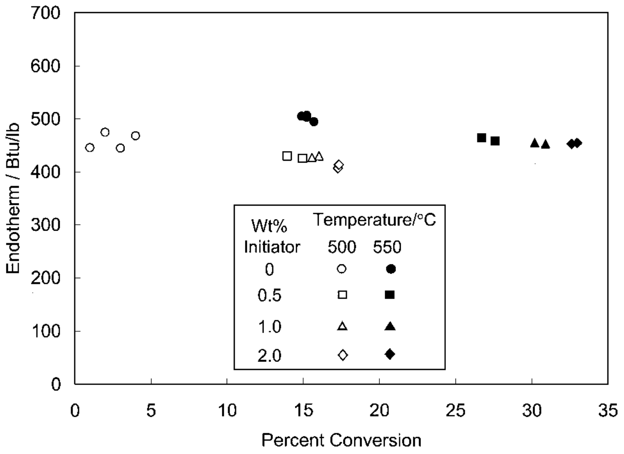

Fig. 5 Endotherm obtained from *n*-heptane cracking (initiated and thermal) as a function of percent of the fuel cracked.

When initiator is added to the fuel, Figs. 3 and 4 show that there is not a significant change in the distribution of products. The major products observed with initiator still center around the C_2 and C_3 mixture of alkanes and alkenes. The overall similarity of the products observed with and without initiator suggest that the addition of initiator has only increased the cracking rate and has not changed the cracking mechanism. This is consistent with the function of the initiator that was already discussed.

The overall effectiveness of using initiated cracking as a cooling mechanism is greatly dependent on the endotherm produced by the reaction. To evaluate this parameter, we used the product distribution to calculate the endotherm of the cracking reaction as a function of percent of fuel cracked at reaction temperatures of 500 and 500°C (the concentrations of the individual products were low at 450°C; we did not include endotherms at this temperature). These values, which include both initiated and noninitiated cracking, are shown in Fig. 5. At 500°C with no initiator, we obtained cracking levels ranging from 2 to 5% and endotherms of between 440 and 470 Btu/lb. When we added initiator at the same temperature, the figure shows that the percent cracking increased significantly, reaching a level of about 17% when 2.0 wt% initiator was injected. In addition, the figure shows that the endotherm was about 410 Btu/lb for 2.0 wt% initiator and about 425 Btu/lb for the lower initiator concentrations. At a reaction temperature of 550°C, the figure shows that without initiator we obtained a cracking level of 15% and an endotherm of 505 Btu/lb. When we added initiator, the cracking levels again increased significantly, reaching a value of 33% at 2.0 wt% addition. At this level the figure shows that the endotherm is about 440 Btu/lb, which is somewhat lower than the baseline value measured without initiator.

Overall, the data are consistent with our suggestion that the initiator only accelerates the reaction rate and does not alter the other steps in the cracking mechanism. Although the initiator increased the *n*-heptane conversion by factors of two or three, it did not significantly affect the product distribution or reaction endotherm.

Cracking of Branched Hydrocarbon Fuels

One of our research objectives was to evaluate the overall thermal cracking rates and effectiveness of the initiator on branched hydrocarbon fuels. Branched fuels are potentially attractive fuels because a branched hydrocarbon has a lower freezing point than the normal paraffin with the same molecular weight.

The results of tests using 2,2,4-trimethyl pentane (isooctane) as our model fuel are shown in Fig. 6. Comparison of the results obtained in this figure to those presented in Fig. 2 lead to two important conclusions. First we see that the cracking rates at 500 and 550°C measured for the branched paraffin without initiator are much lower than the results obtained with *n*-heptane (Fig. 2). The rates measured for *n*-heptane at 500 and 550°C are 0.085 and 0.44 moles/h cc, whereas those measured for 2,2,4-trimethyl pentane are only 0.045 and 0.23 moles/h cc respectively at these temperatures.

The second difference is that the initiator has very little effect on the branched paraffin, whereas it had significant effects on the normal alkanes. Figure 2 shows that the initiator produced significant increases in rate of *n*-heptane cracking at all reaction temperatures. For example at 500 and 550°C, we obtained incremental increases of between 0.4 and 0.5 moles/h cc with 2.0 wt% initiator. By contrast, Fig. 6 shows that at 500 and 550°C addition of initiator to 2,2,4-trimethylpentane fuel only increased the reaction rate by a maximum of 0.15 moles/h cc. We conclude from these results that isoparaffin fuels undergo thermal cracking at lower rates than normal paraffins of similar molecular weight under these reaction conditions and that isoparaffins are less affected by the initiator.

In addition to cracking at lower rates, we found that the products obtained in the cracking of this isoparaffin were significantly different from those measured with *n*-heptane. The products obtained during the test of 2,2,4-trimethyl pentane are shown in Fig. 7. This figure shows that cracking of 2,2,4-trimethyl pentane produces primarily four compounds, which we identified as methane, propene, isobutane and isobutene. Although this product distribution is significantly different from the products of normal paraffin cracking (Figs. 3 and 4), we see again that the initiator has no significant effect on the products formed. We calculated the endotherm produced from this product distribution and found that it was approximately 300 Btu/lb, compared to the values of 400–500 Btu/lb obtained with *n*-heptane. We thus conclude that branched hydrocarbons undergo thermal cracking at lower rates relative to normal alkanes, the cracking rates are less subject to enhancement by our initiator compared to *n*-heptane, and finally, the endotherm resulting from cracking is significantly lower than that produced with normal alkanes.

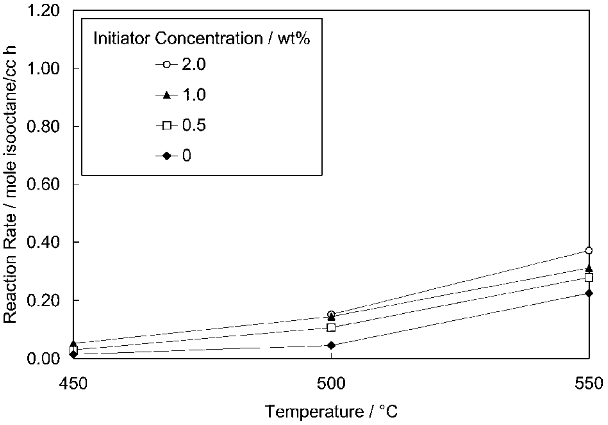

Fig. 6 Cracking rates obtained for 2,2,4-trimethyl pentane with up to 2.0 wt% initiator added.

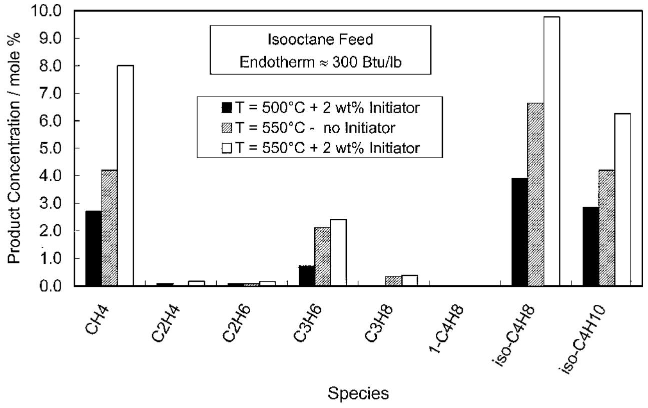

Fig. 7 Product distribution obtained from cracking 2,2,4-trimethyl-pentane with and without initiator.

Conclusions

We carried out laboratory investigations to determine if the rate of thermal cracking of both normal and isoparaffins could be accelerated by adding a chemical initiator to the fuel. We identified several compounds that produce significant increases in the rates of thermal cracking of normal alkanes at temperatures of 450, 500, and 550°C and at pressures of 37 atm. The most active compound we identified is significantly more active than commercially available initiators such as AIBN. It is soluble in normal paraffins, allowing it to be either injected directly into the fuel or dissolved in the fuel tank. In addition, the compound is stable and is not highly toxic in its concentrated form. We found that at all temperatures the addition of up to 2 wt% percent of this compound produced measurable increases in cracking rate. For example at 500°C, this initiator increased the rate of *n*-heptane cracking by a factor of six, whereas at 550°C the initiator produced over a factor of two improvement in rate. The product distributions obtained with and without initiator are similar, indicating that the initiator only accelerates the cracking rate and does not alter the overall thermal cracking mechanism. We calculated an endotherm of 400–500 Btu per pound of *n*-heptane cracked and found that this value was independent of percent fuel reacted. Finally, we found that the model isoparaffin fuel, 2,2,4-trimethylpentane, cracks at a lower rate, is less affected by the initiator, and produces a lower endotherm relative to the normal paraffin fuels.

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