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Enhancement of the Destruction of Propane in a Low-Temperature Plasma by the Addition of Unsaturated Hydrocarbons: Experiment and Modeling

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The oxidative destruction of propane at low temperature (~150 °C) in a nonthermal, atmospheric pressure plasma can be significantly enhanced without the use of a catalyst by the simple addition of an unsaturated alkene. An enhancement in the destruction of propane of up to 45% can be achieved by the addition of propene. Propene acts as a supply of OH radicals, which accelerate the breakdown of the propane. Ethene also enhances the destruction of propane but to a more limited extent. The experimental results are interpreted by chemical modeling, which is used to elucidate the reaction mechanisms.

Introduction

The oxidative and nonoxidative conversion of saturated hydrocarbons (especially methane) into cleaner fuels such as hydrogen or methanol or into higher value products or feedstocks such as formaldehyde, ethene, and ethyne is a topic of considerable interest in terms of reducing greenhouse emissions and providing enhanced sustainability. Because of the large C−H and C−C bond strengths, these conversions often only take place under extreme conditions of temperature and pressure, which place challenging demands on process technologies and are very energy intensive. Research continues to find efficient catalysts or alternative technologies that will permit operation at lower temperatures. The use of catalysts at elevated temperatures for hydrocarbon conversion commonly leads to problems of coking and sintering. Plasma methods have recently been employed to "reform" hydrocarbons at low temperature into synthesis gas (a mixture of CO and H_2), alcohols, and higher hydrocarbons;[1−5] in some of these studies, the plasma discharge has been combined with a catalyst. Choudhary et al.[6] have shown how the conversion of methane over a zeolite catalyst at 400−600 °C can be enhanced by the coaddition of an alkene or higher alkane. Plasma methods have also been used to destroy hydrocarbon contaminants in air by complete oxidation into CO and CO_2. We have investigated the plasma destruction of small concentrations of hydrocarbons such as methane, propane, propene, benzene, and toluene in atmospheric pressure air with and without catalysts.[7−9] In this Article, we demonstrate how the plasma destruction of a saturated alkane, propane, can be enhanced at a low temperature (~150 °C) without the use of a catalyst by the coaddition of an unsaturated alkene, either propene or ethene. The experimental results are interpreted by chemical modeling, which is used to elucidate the reaction mechanisms.

Experimental Section

The experimental configuration used in this study has been described previously.[7,9] Specifically, 100 ppm of an atmospheric pressure mixture of propane and propene (mixing ratio 0.2−9.0) in synthetic air (20% O_2, 80% N_2) was flowed at 1 L min^{-1} and passed through a low temperature, dielectric plasma reactor packed with $BaTiO_3$ beads. The plasma reactor was powered by a high frequency AC voltage with electrical powers between 0.2 and 1 W. The detection and quantification of the end-products of the plasma processing is achieved using FTIR spectroscopy. A schematic diagram of the experimental setup can be found in Figure 1.

Modeling

To support the experimental work, a chemical model for processing a mixture of propane and propene was developed using CHEMKIN II. It is assumed that there is uniform processing of the gas as it passes through the reactor. During each half-cycle, the microdischarge current pulses create active species, which then go on to initiate or continue the chemistry. In our model,[10] a fresh supply of the active species is injected into the reaction mixture at each pulse, and the chemistry is allowed to continue until the next pulse. Packed-bed dielectric plasma rectors have inherently low reduced electric field strengths, and the majority of the energy in the discharge goes into vibrational and electronic excitation of the nitrogen molecules, a small amount into O_2 dissociation, and almost none into N atom production. Thus, in the model, we only consider the production of oxygen atoms as in a previous study of propene destruction in a simulation of diesel exhaust remediation.[10] To determine the concentration of oxygen atoms produced in each plasma pulse, we adjusted the O atom concentration to obtain the best fit to the experimental data for a 50:50 mixture of propane and propene at a specific energy density of 35 J L^{-1}. This value was then used in all of the simulations. The reaction mechanism was adapted from that used in Hill et al.;[11] the majority of the breakdown routes for propane and propene follow the same pathways. However, additional reactions were needed to describe the initial breakdown of propene by the primary and secondary active species formed in the plasma. The mechanism is detailed in the discussion.

Results

Figure 2 shows the destruction of both propane and propene in mixtures of varying composition as a function of the specific input energy, SIE (electrical power supplied to the plasma/total gas flow rate). There is substantial enhancement of the propane destruction as more propene is added to the mixture, but the

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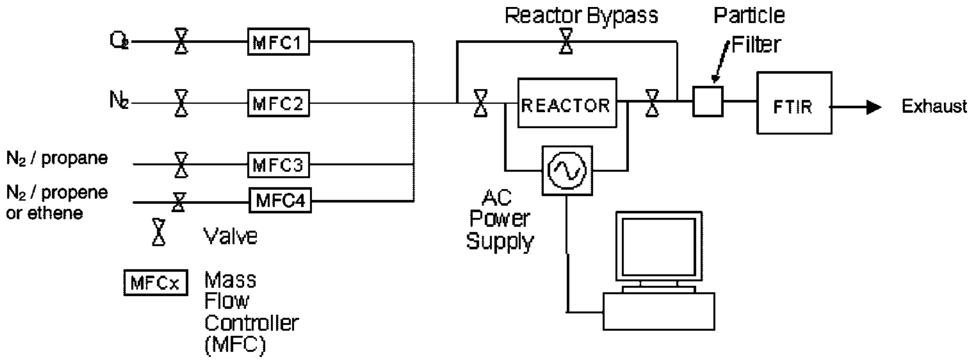

Figure 1. Experimental configuration for the plasma destruction of hydrocarbon mixtures.

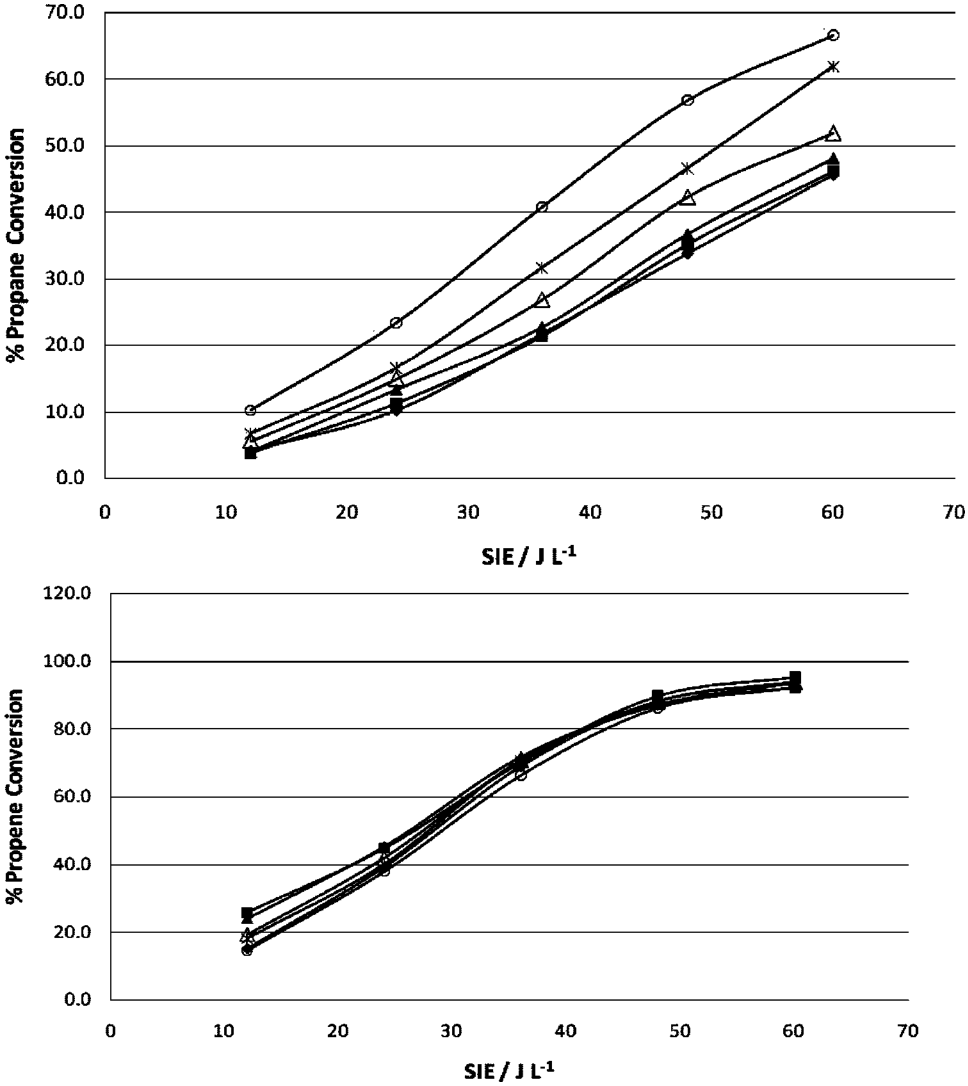

Figure 2. Plasma destruction of propane (upper panel) and propene (lower panel) as a function of specific input energy, SIE, for different initial concentration ratios of propane and propene. In all cases, the total hydrocarbon concentration was 100 ppm (balance synthetic air) at a flow rate of 1 L min^{-1}. ◆ propane only; ◆ propene only; ■ C_3H_8:C_3H_6 = 9.0; ▲ C_3H_8:C_3H_6 = 2.3; Δ C_3H_8:C_3H_6 = 1.0; × C_3H_8:C_3H_6 = 0.6; and ○ C_3H_8:C_3H_6 = 0.2. The lines are added to distinguish the different experiments and do not represent the results of any simulations.

destruction of the propene is unaffected by the addition of propane. The largest enhancement of propane destruction is seen at 60 J L^{-1} where a destruction of 67% is achieved for a mixing ratio of 0.2 as compared to 46% for pure propane, an enhancement of ~45%.

Figure 3 shows the effect of changing the temperature from 120 to 240 °C for a mixture with a propane:propene ratio of 0.2 and a SIE of 48 J L^{-1}. Propene destruction improves only slightly from ~80% to ~90% as the temperature increases, but the change in propane destruction both alone and in a mixture is more dramatic, increasing by ~20% as the temperature is raised. Propane destruction can be increased by ~20% by either adding propene to the gas mixture without changing the temperature or raising the temperature by ~120 °C. An increase in temperature leads to increased energy input to enhance the destruction, but the addition of a secondary gas does not require any additional energy cost to achieve the same gain in destruction.

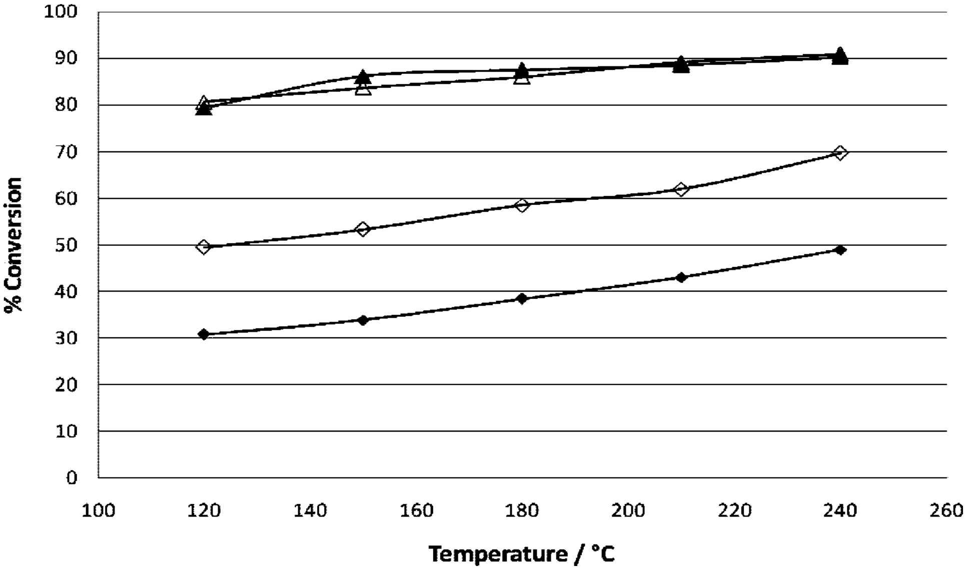

Figure 3. The effect of temperature on the experimentally measured propane and propene destruction from separate processing (100 ppm) and in a mixture (C_3H_8:C_3H_6 concentration ratio of 0.2) at constant SIE = 48 J L^{-1}. ◆ propane destruction alone; ◇ propane destruction in mixture; ▲ propene destruction alone; and Δ propene destruction in mixture. The lines are added to distinguish the different experiments and do not represent the results of any simulations.

To investigate the generality of this effect, we also studied the enhancement of propane destruction in mixtures with ethene as shown in Figure 4. Propane destruction increases with raising SIE and the initial concentration ratio of propane and ethene but not as dramatically as was seen for mixtures of propane with propene. At an SIE of 60 J L^{-1}, propane destruction alone reaches 46% and with a mixture (C_3H_8:C_2H_4 ratio = 0.14) 58% destruction is achieved. Ethene addition provides an enhancement of ~25% to the propane destruction as compared to values of ~45% seen in mixtures with propene. As was observed for the propane with propene mixtures, there was no change in the ethene destruction with changing mixing ratios.

Figure 5 shows the effect of changing the temperature from 120 to 240 °C for a mixture with a propane:ethene ratio of 0.22 and a SIE of 48 J L^{-1}. The ethene destruction shows an increase of ~20% over the temperature range studied and is unaffected by the addition of propane. The propane destruction however is affected by the addition of ethene and is improved by ~8% over the whole temperature range tested. The temperature increase from 120 to 240 °C improves the destruction of propane by ~20% regardless of whether the propane is processed separately or with ethene.

The products of the plasma processing of both propane and propene in air are the same, carbon monoxide, CO, carbon dioxide, CO_2, and trace amounts of formaldehyde, HCHO. Processing of a mixture of propane and propene produces only CO and CO_2. Plasma processing of ethene in air produces only CO and CO_2, and, in combination with propane, the products are unchanged.

A computer simulation was performed for propane and propene mixture processing in air using the mechanisms developed previously[10,11] with the addition of some further reactions to describe the ethene chemistry. The model was run under the same initial ratio conditions as the experiments so a direct comparison could be made. Figure 6 shows these results at a fixed temperature of 150 °C. As compared to Figure 2, the simulation shows reasonable agreement with the experimental data for propene destruction, which increases from ~25% to ~90% over the SIE range used. However, the simulation gives more separation between the different concentration ratios than is observed experimentally. The simulated propane destruction show a trend similar to that of the experimental results of Figure 2 when the concentration ratios are varied. At the largest SIE modeled (56 J L^{-1}), the addition of propene increases the propane destruction by ~20%, which is also observed in the experiments. Exact agreement with the experimental data is not obtained, however, as the simulation underestimates the propane destruction. However, a similar trend is definitely reproduced; a larger propene initial concentration enhances the propane destruction.

Discussion

These observations must be rationalized entirely in terms of the gas-phase chemistry taking place in the plasma as previous work[12] has shown no heterogeneous catalytic effects take place upon the barium titanate beads and there is no destruction of the hydrocarbon without a discharge. In a nonthermal, atmospheric pressure plasma, there is a significant disequilibrium between the electron temperature (commonly ≥10 000 K) and that of the heavy particles, which is typically close to ambient (≤150 °C). In an oxidative environment such as in the present work, electron−molecule collisions occur with oxygen molecules more commonly and with higher efficiency than with the hydrocarbon species because of the extreme concentration differences. This means that the chemistry is primarily initiated by reactions of the hydrocarbon species with oxygen atoms created in the discharge by dissociation of O_2. The mechanisms for oxidative plasma decomposition of propane and propene are well established.[10,11,13] The reaction of atomic oxygen proceeds via hydrogen atom abstraction

$$O + C_3H_8 \rightarrow OH + C_3H_7 \qquad (1)$$

in a slow reaction ($k = 7.3 \times 10^9$ cm^3 mol^{-1} s^{-1} at 150 °C).[14] In contrast, the overall reaction of O atoms with propene

$$O + C_3H_6 \rightarrow \text{products} \qquad (2)$$

is considerably faster ($k = 3.1 \times 10^{12}$ cm^3 mol^{-1} s^{-1} at 150 °C)[14] and is a more effective source of OH radicals than reaction 1 or subsequent reactions of the products with additional atomic

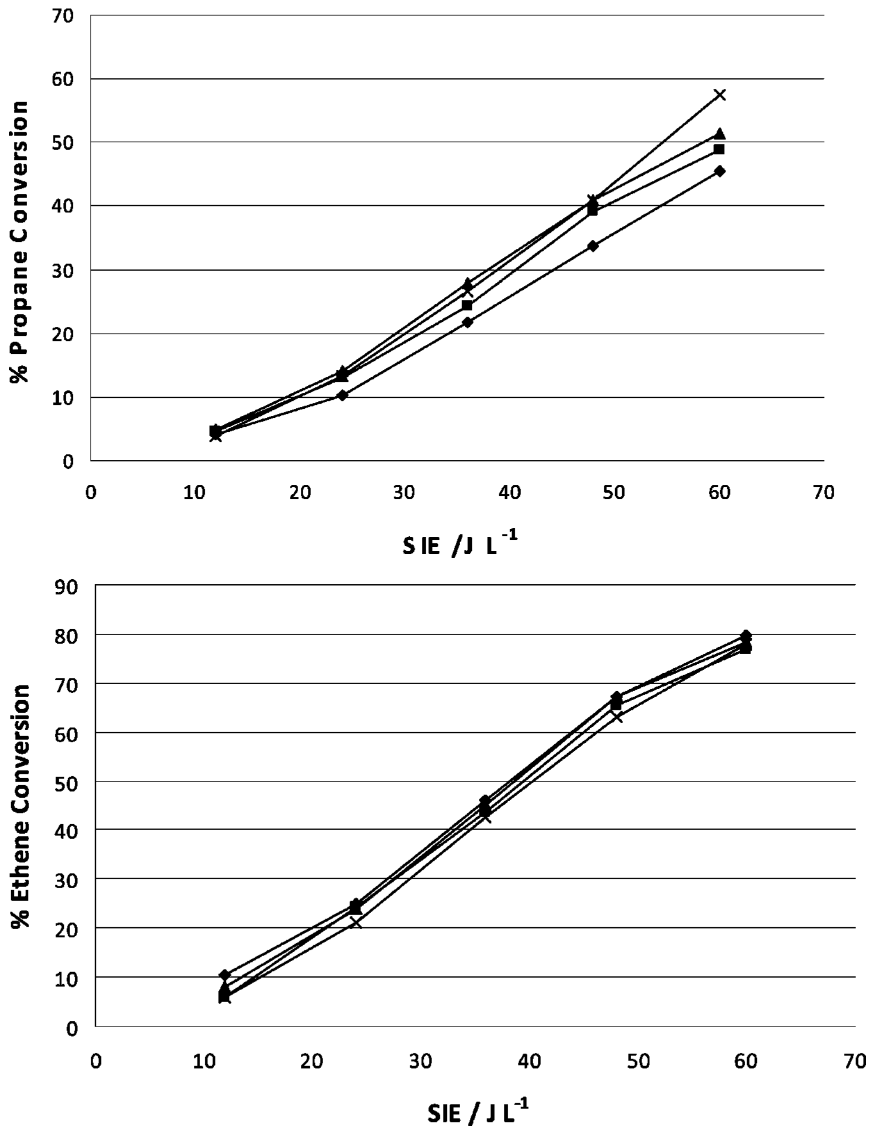

Figure 4. Plasma destruction of propane (upper panel) and ethene (lower panel) as a function of specific input energy, SIE, for different initial concentration ratios of propane and ethene. In all cases, the total hydrocarbon concentration was 100 ppm (balance synthetic air) at a flow rate of 1 L min^{-1}. ◆ propane only; ◆ ethene only; ■ C_3H_8:C_2H_4 = 0.57; ▲ C_3H_8:C_2H_4 = 0.25; and × C_3H_8:C_2H_4 = 0.14. The lines are added to distinguish the different experiments and do not represent the results of any simulations.

TABLE 1: Rate Coefficients Calculated for Propane, Propene, and Ethene Reaction with Oxygen Atoms at 120 and 240 °C[a]

	rate coefficient/cm^3 mol^{-1} s^{-1}	
reaction	120 °C	240 °C
$C_3H_8 + O \rightarrow$ products + OH	3.0×10^9	5.6×10^{10}
$C_3H_6 + O \rightarrow$ products + OH	3.0×10^{12}	3.5×10^{12}
$C_2H_4 + O \rightarrow$ products	8.1×10^{11}	1.4×10^{12}

[a] Rate data taken from NIST.[14]

oxygen. Thus, in the mixtures, addition of propene to propane will provide an efficient source of OH radicals, which will then more rapidly react with the propane.

$$OH + C_3H_8 \rightarrow H_2O + C_3H_7 \qquad (3)$$

Reaction 3 has a much larger rate constant at 150 °C ($k = 1.4 \times 10^{12}$ cm^3 mol^{-1} s^{-1}) and is considerably faster[14] than is reaction 1. The temperature dependence that was observed in Figure 3 can also be related to changes in the rate constants for oxygen atoms with the hydrocarbons. For propane, the rate constant increases by a factor of ~20 in going from 120 to 240 °C, whereas that for propene only changes by ~1.2.[14] Thus, the enhancement seen with increasing temperature for pure propane and for the mixture of propane and propene reflects the temperature dependence of reaction 1. The reduced enhancement of propane destruction in mixtures with ethene comes from the lower rate constant for the reaction

$$O + C_2H_4 \rightarrow \text{products} \qquad (4)$$

which has a rate constant value ($k = 8.4 \times 10^{11}$ cm^3 mol^{-1} s^{-1} at 150 °C)[14] less than that for reaction 2. As with propene, the temperature effect on reaction 4 is minimal as compared to that on reaction 1, increasing by a factor of ~1.7 over the temperature range studied. The calculated rate constants at both 120 and 240 °C are given in Table 1.

Conclusions

We have shown that the simple addition of an alkene assists the destruction of propane in plasma processing at low temperature without the use of any catalyst. This methodology could

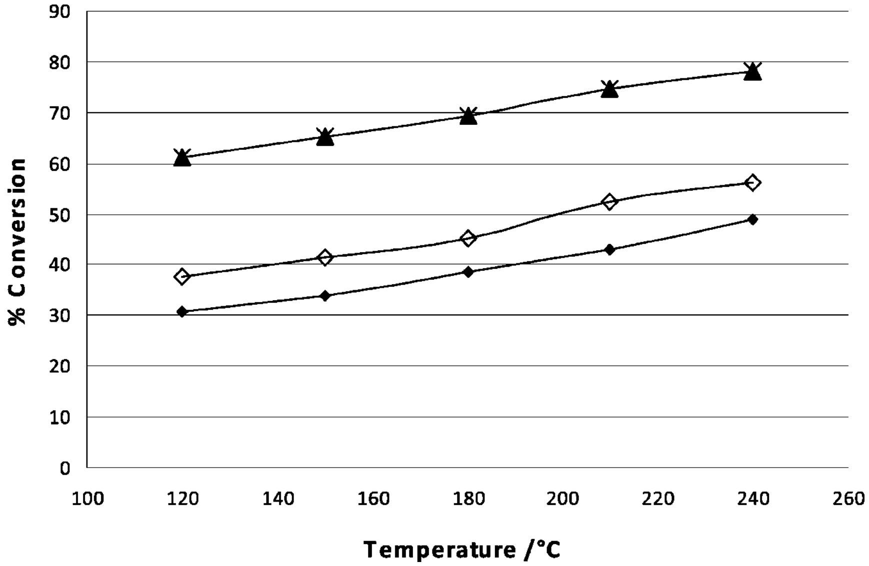

Figure 5. The effect of temperature on the experimentally measured propane and ethene destruction from separate processing (100 ppm) and in a mixture (C_3H_8:C_2H_4 concentration ratio of 0.22) at constant SIE = 48 J L^{-1}. ◆ propane destruction alone; ◇ propane destruction in mixture; ▲ ethene destruction alone; and × ethene destruction in mixture. The lines are added to distinguish the different experiments and do not represent the results of any simulations.

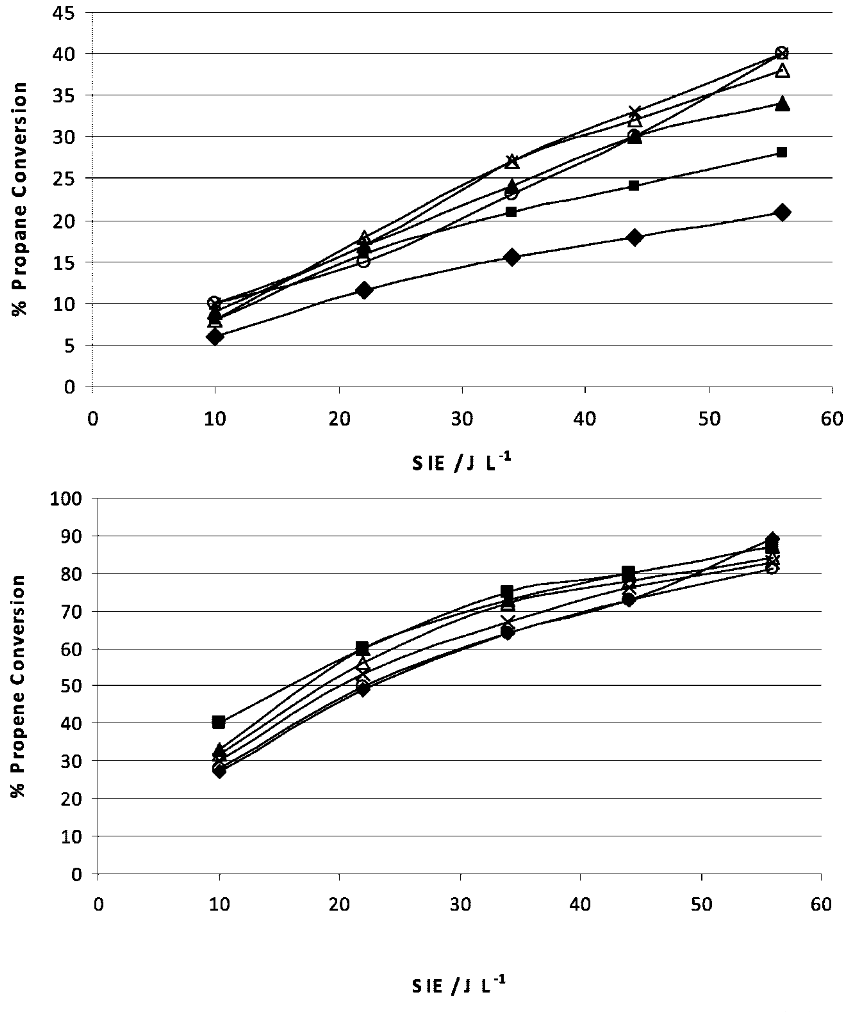

Figure 6. Simulated destruction of propane (upper panel) and propene (lower panel) as a function of SIE at 150 °C. ◆ propane only; ◆ propene only; ■ C_3H_8:C_3H_6 = 9.0; ▲ C_3H_8:C_3H_6 = 2.3; Δ C_3H_8:C_3H_6 = 1.0; × C_3H_8:C_3H_6 = 0.6; and ○ C_3H_8:C_3H_6 = 0.2. The lines are added to distinguish the different simulations and do not represent the experimental results.

be applied to the oxidative conversion of any hydrocarbon that is normally inefficient because of low reaction rates for the initial attack by atomic oxygen by giving a supply of OH radicals from the faster reaction of the coadditive with the oxygen. In fact, the coadditive does not then necessarily need to be an alkene but any compatible organic species that will act as a fast source of OH radicals. It is also apparent that a modest increase in temperature will additionally enhance the destruction of the hydrocarbon.

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