

# Effect of Methane and Hydrogen During Thermal Cracking of Light Hydrocarbons

K. M. Sundaram,  
J. M. Fernandez-Baujin  
Lummus Crest Inc.  
Bloomfield, NJ 07003

The pyrolysis reactors designed in the past for the production of ethylene through the thermal cracking of hydrocarbons were provided with feedstock flexibility for either a variety of light hydrocarbon feedstocks or naphthas/gas oils. In the last decade, however, the trend of available feedstocks has motivated olefins producers to consider the implementation of complete feedstock flexibility, which has been already successfully incorporated in many of the existing SRT III pyrolysis reactors built in the United States (Solomon, 1977; Sumner and Fernandez-Baujin, 1983).

Gaseous feedstocks are normally found as a mixture of light hydrocarbons containing hydrogen and methane, which have been identified as essentially nonreactive impurities. To design and efficiently operate pyrolysis reactors using the gaseous feeds, it is essential to have a good knowledge of the kinetics involved during cracking and the achievable product distribution.

Numerous computerized kinetic models have evolved in recent years (Allara and Edelson, 1975; Dente et al., 1979; Sundaram and Froment 1977a,b, 1978). However, the required kinetic constants are not known with sufficient accuracy to study the effect of hydrogen and methane in the pyrolysis of ethane, propane, and butanes. To obtain the results discussed in this paper, experiments were conducted to determine the effect of hydrogen and methane during the pyrolysis of light hydrocarbons. Modeling was used to guide the experimental program.

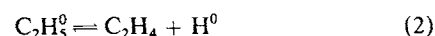
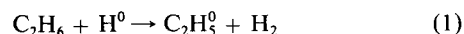
Kunugi et al. (1974), Susu and Ogunye (1979), and Zhorov et al. (1977) have reported that the addition of hydrogen to naphthas results in an ethylene yield enhancement during pyrolysis. The hydrogen reacts with high molecular products such as aromatics. The reaction with hydrogen followed by the pyrolysis reaction of the products is responsible for the higher ethylene and the lower yields of liquid products (C5+ fraction of the effluent).

In the pyrolysis of ethane, however, the yield of liquid products is very small (1 to 2 wt. % of feed). Does the presence of hydrogen in the ethane feed have the same impact as in the

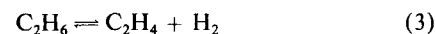
naphtha feed? What is the impact of the methane present in ethane feed? What are the trends in propane and LPG feeds?

## Pyrolysis of Ethane in the Presence of Methane and Hydrogen as Feed Impurities

The main pathway to ethylene production during the pyrolysis of ethane is given below,



The corresponding molecular reaction is



which accounts for more than 90% of the reactions in ethane pyrolysis (Sundaram and Froment, 1977).

The thermodynamic properties of many radicals are rarely available and are less accurate than those of molecular species. Furthermore, when a radical reaction mechanism is used, it is necessary to include in the model many more reactions than reactions 1 and 2 given above. In the present investigation, however, the effect of hydrogen and methane was qualitatively predicted with a molecular reaction mechanism represented by reaction 3. This approach was used to guide the experimental work.

Using the free energy of formation data given by Stull et al. (1969) for the reactants and the products of reaction 3, the thermodynamic equilibrium constant  $K_p$  and the equilibrium conversion  $X$  can be calculated as follows:

$$K_p = \frac{P_{\text{C}_2\text{H}_4} \cdot P_{\text{H}_2}}{P_{\text{C}_2\text{H}_6}} \quad (4)$$

and

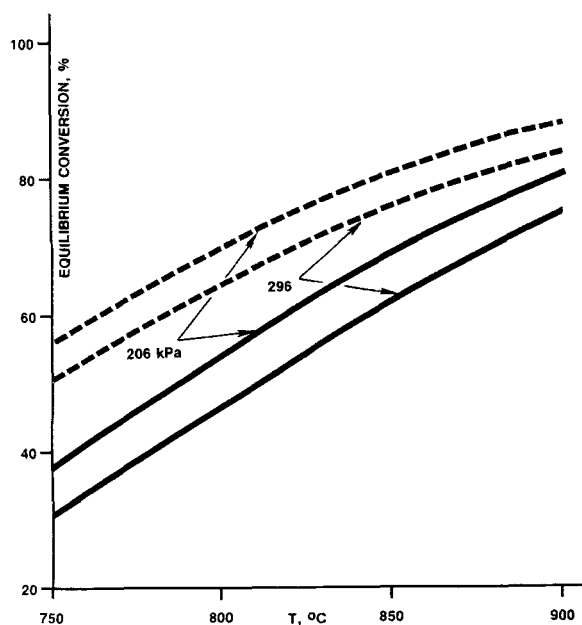
$$K_p = \frac{X * (X + \alpha)}{(1 - X)} * \frac{F_o * P_t}{F_t} \quad (5)$$

When calculating the total molar flow rate, the expansion factor  $\epsilon$  is assumed to be independent of conversion.  $\epsilon$  is defined as the number of moles formed per mole of ethane converted. A value of 2 has been reported by Froment et al. (1976) and is also confirmed by the experimental work reported in this paper.

In Figure 1, ethane equilibrium conversion vs. temperature and total pressure for two hydrogen concentrations at constant dilution ratio is illustrated. In ethane pyrolysis, the equilibrium conversion decreases with increasing system pressure. The addition of hydrogen also reduces the equilibrium conversion. In fact, Schutt (1959) reported that in some industrial ethane crackers ethylene yields were lower than expected due to the side reactions associated with the high hydrogen concentration at the reactor outlet. In summary, addition of hydrogen during the pyrolysis of ethane decreases the ethylene yield, in contrast to the ethylene yield increase observed when hydrogen is added to liquid feedstocks (naphthas and gas oils).

When methane is added to the ethane feed, it acts as an inert according to reaction 3. The equilibrium conversion can be calculated with Eq. 5. In this case, methane and steam are used to calculate the dilution ratio. There is no effect on the equilibrium conversion when part or all of the dilution steam is replaced by methane at a given total dilution ratio.

It should be noted, however, that the actual ethylene yield from pyrolysis is determined by kinetics considerations of the reactor instead of thermodynamic equilibrium.



**Figure 1. Equilibrium ethane conversions as a function of temperature, pressure and hydrogen content in feed.**

$C_2H_6 \rightleftharpoons C_2H_4 + H_2$   
 $(H_2 + H_2O)/C_2H_6 = 1.71 \text{ mol/mol}$   
 --- 0 wt. %  $H_2$  in  $C_2H_6$   
 — 5 wt. %  $H_2$  in  $C_2H_6$

## Effect of Addition of Methane and Hydrogen on Hydrogen-Methyl Radical Reaction

The hydrogen-methyl radical reaction must be considered when handling hydrogen and methane containing feedstocks.



The equilibrium constant data have been reported by Allara and Edelson (1975) as shown below,

$$K_p = \frac{P_{CH_4} * P_{H_2}}{P_{H_2} * P_{CH_3}} = 21.47 \exp(-310.3/T) \quad (7)$$

The equilibrium constant is not very sensitive to temperature:  $K_p = 16.29$  at  $850^\circ\text{C}$  vs.  $K_p = 16.08$  at  $800^\circ\text{C}$ .

In general, the ratio of  $H^\bullet$  to  $CH_3^\bullet$  radicals varies from 0.1 to 10 in ethane cracking (Sundaram and Froment, 1978 a,b). The typical value at the reactor outlet is close to one. Assuming as an approximation that the ratio of the radicals is constant, it can be concluded qualitatively that the addition of hydrogen increases the methane yield. Conversely, the addition of methane increases the hydrogen yield. Therefore, the effect of hydrogen in ethane cracking can be compensated with the addition of methane. However, because of the differences in molecular weights, eight weight units of methane are required per weight unit of hydrogen.

## Experimental Procedure

The experimental work was conducted in the Lummus Profile Controlled Pyrolysis pilot reactor (PCP unit). This is the fifth generation of pyrolysis pilot plants developed by Lummus (Fernandez-Baujin and Solomon, 1975). The pyrolysis yields obtained in this unit have closely reproduced the data obtained in SRT I, II, III, and IV commercial reactors cracking ethane, propane, butanes, naphthas, and gas oils.

The unit consists of a small-diameter tubular reactor. The pyrolysis coil has been designed to allow control of the process gas temperature along the length of the coil as well as the hydrocarbon partial pressure of the reacting mixture. The PCP unit permits an accurate simulation of the commercial coil performance.

The reactor effluent is rapidly quenched, directly and/or indirectly, and is sent to an elaborate sampling system where the different fractions are separated and collected at optimal temperatures and pressures. The effluent is analyzed routinely for  $H_2$ ,  $C_1$  to  $C_5$ 's, detailed breakdown of pyrolysis gasoline, and fuel oil. The operation of the unit is continuously monitored by an on-line gas chromatograph.

The feedstocks used in this experimental work are summarized in Table 1 together with the objectives of each series of tests.

## Ethane Pyrolysis—Experimental Program

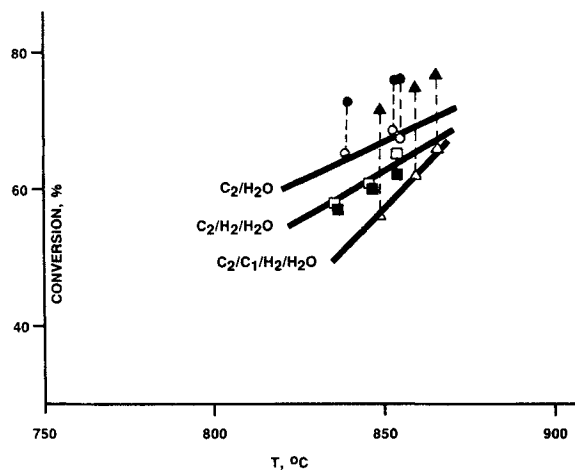
In cracking ethane-rich mixtures, the bulk residence time of the reaction zone was about 0.5 s and the total outlet reactor pressure was 296 kPa. absolute. The ethane conversion at the reactor outlet ranged from 57 to 69%. Only experimental runs with overall material and hydrogen balance closures higher than 98% were selected for this data evaluation.

**Table 1. Summary of Planned Experiments**

No.	HC Feed	Diluents	Dilution mol/mol HC	COP kPa	Purpose of Experiment
1	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O	1.8	296	Base case and verify reproducibility of previous experiments
2	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O + H <sub>2</sub>	1.8	296	Effect of hydrogen on C <sub>2</sub> H <sub>6</sub> cracking. Is H <sub>2</sub> a diluent or a reactant?
3	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O + H <sub>2</sub> + CH <sub>4</sub>	1.8	296	Effect of hydrogen and methane on C <sub>2</sub> H <sub>6</sub> cracking. Is CH <sub>4</sub> a diluent?
4	C <sub>2</sub> H <sub>6</sub> + C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub> O + H <sub>2</sub> + CH <sub>4</sub>	1.8	206	Effect of H <sub>2</sub> & CH <sub>4</sub> on cocracking of C <sub>2</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub>
5	C <sub>2</sub> H <sub>6</sub> + C <sub>3</sub> H <sub>8</sub> + nC <sub>4</sub> H <sub>10</sub> + iC <sub>4</sub> H <sub>10</sub>	H <sub>2</sub> O + H <sub>2</sub> + CH <sub>4</sub>	1.8	206	Effect of C <sub>4</sub> addition
6	C <sub>2</sub> H <sub>6</sub> + C <sub>3</sub> H <sub>8</sub> + nC <sub>4</sub> H <sub>10</sub> + iC <sub>4</sub> H <sub>10</sub>	H <sub>2</sub> O + CH <sub>4</sub>	1.8	206	Effect of H <sub>2</sub> on LPG mixture and verification of results obtained with ethane

HC: hydrocarbon

The reactor outlet ethane conversions are plotted as a function of outlet gas temperatures in Figure 2 for various concentrations of methane and hydrogen in the feed. The molar dilution ratio  $\delta$  was approximately constant in all experiments. The equilibrium conversions are also plotted in Figure 2 for reference. When only dilution steam is used, the experimental conversion is significantly less than that corresponding to equilibrium. A similar conclusion is derived for the cases where hydrogen and methane are added to the ethane feed. However, when only hydrogen is added to ethane, the experimental ethane conversions are almost identical to those corresponding to equilibrium.



**Figure 2. Experimental and equilibrium conversions for ethane to ethylene and hydrogen in various feeds.**

Runs	Feed	COP kPa	H <sub>2</sub> wt. %	$\frac{H_2 + C_1 + H_2O}{C_2}$ mol/mol
●, ○	C <sub>2</sub> /H <sub>2</sub> O	296	0	1.71
■, □	C <sub>2</sub> /H <sub>2</sub> /H <sub>2</sub> O	296	5	1.71
▲, △	C <sub>2</sub> /C <sub>1</sub> /H <sub>2</sub> /H <sub>2</sub> O	296	4.3	1.85

C<sub>2</sub>H<sub>6</sub> = C<sub>2</sub>H<sub>4</sub> + H<sub>2</sub>  
 ●, ■, ▲ Equilib. values  
 ○, □, △ Exp. values

### Product Distribution—Ethane Cracking

The addition of hydrogen depresses the ethylene yield by about 1 to 2 wt. % of feed when compared to results from cracking ethane only in the presence of dilution steam. The comparison is made at similar ethane conversions. In the case of the hydrogen addition, the methane yield is also higher by about 1 wt. % of feed. High molecular weight products such as toluene and fuel oil are found in the reactor outlet in extremely small quantities. This finding suggests that these compounds are rapidly hydrogenated. However, the observed lower ethylene yield still suggests that the reverse path of reaction 3 has the predominant effect.

The ethylene yields from the feed containing ethane, methane, and steam fall between those from only ethane and steam on the high side and those from the mixture of ethane, hydrogen, and steam on the low side.

### Effect of the Addition of Methane and Hydrogen During Pyrolysis of LPG

Experimental pyrolysis tests were also conducted by adding methane and hydrogen to mixtures of ethane and propane and ethane, propane, and butanes. The achieved yield slates and the

**Table 2. Qualitative Trends for Major Products on Effects of Addition of Hydrogen and Methane to Various Feeds**

Yield of	Addition of H <sub>2</sub> and CH <sub>4</sub> on Cracking of		
	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub> - C <sub>3</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>6</sub> - C <sub>3</sub> H <sub>8</sub> - nC <sub>4</sub> - iC <sub>4</sub> *
H <sub>2</sub>	—	↓	↓
CH <sub>4</sub>	↑	↓	↓
C <sub>2</sub> H <sub>4</sub>	↓	↓	↓
C <sub>3</sub> H <sub>6</sub>	↓	↓	↓
C <sub>4</sub> + C <sub>4</sub> +	↓	↓	↓
Benzene	—	↓	↓
C <sub>5</sub> + and C <sub>6</sub> +	↓	↓	↓

\*Includes cocracking effect

Methane acts almost like a diluent in C<sub>2</sub>H<sub>6</sub> cracking

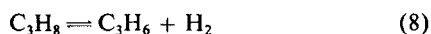
↑ increases

↓ decreases

cocracking conversion data were extensively studied. The trends of the major products for the various feedstocks are summarized in Table 2.

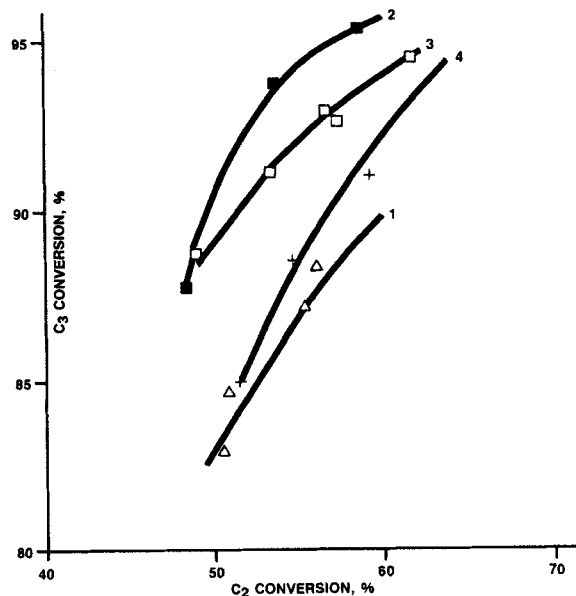
## Feed Conversion

Propane conversion data are plotted as a function of ethane conversion in Figure 3 to illustrate the effect of the addition of methane and hydrogen. In the presence of hydrogen, the reverse path of reaction 3 proceeds significantly and thus reduces the ethane conversion. A similar reversible reaction occurs in propane cracking as shown below.



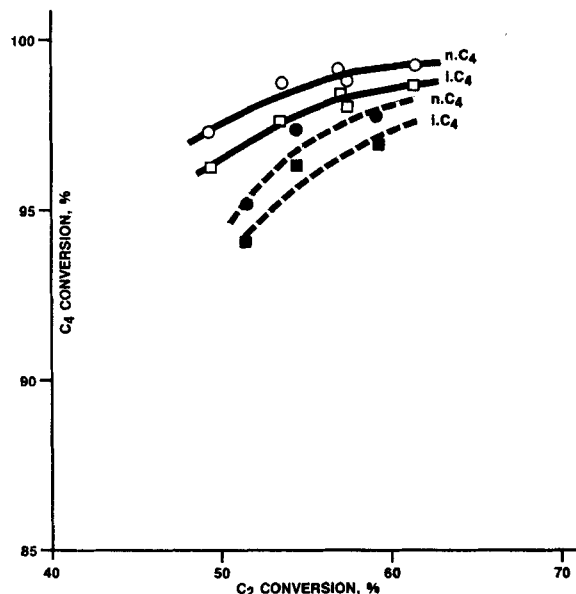
However, the equilibrium constant for propane cracking is higher than that corresponding to ethane cracking. Thus, the addition of hydrogen does not affect the pyrolysis of propane significantly. In conclusion, for a given ethane conversion at the reactor outlet, the propane conversion in the presence of hydrogen will be higher than the propane conversion achieved in the absence of hydrogen. A similar conclusion can be made about butane conversion from the data on systems containing ethane and butanes.

During propane cracking, the yield of ethane is significant. When the feed to the reactor is a mixture of ethane and propane, the ethane yielded by the pyrolysis of propane interferes with the determination of the ethane conversion. However, this is not the case when calculating the propane conversion since the propane yielded during the pyrolysis of ethane is very small. In Figure 3, the true conversions of ethane and propane have been plotted for various feedstocks. In Figure 4, the true conversions of *n*-butane and isobutane have been plotted as a function of the true conversions of ethane. True conversion is defined as follows:



**Figure 3. Comparison of propane conversion as a function of ethane conversion for various feeds.**

△, 1  $\text{C}_2/\text{C}_3 = 60/40$  wt. % + steam only  
 ■, 2  $\text{C}_2/\text{C}_3 = 61/39$  wt. % +  $\text{H}_2$  and  $\text{CH}_4 + \text{H}_2\text{O}$   
 □, 3  $\text{C}_2/\text{C}_3/\text{nC}_4/\text{iC}_4 = 51/20/19/10$  wt. % +  $\text{H}_2 + \text{CH}_4 + \text{H}_2\text{O}$   
 +, 4  $\text{C}_2/\text{C}_3/\text{nC}_4/\text{iC}_4 = 51/20/19/10$  wt. % +  $\text{CH}_4 + \text{H}_2\text{O}$



**Figure 4. Normal and isobutane conversions as a function of ethane conversion.**

Feed ( $\text{C}_2/\text{C}_3/\text{nC}_4/\text{iC}_4 = 51/20/19/10$  wt. %)  
 O, □, — with  $\text{CH}_4$  and  $\text{H}_2$  and steam  
 O, □, --- with  $\text{CH}_4$  and steam

True conversion  
of ethane

$$= \frac{\left( \text{Ethane} \right)_{\text{in feed}} - \left( \text{Ethane} \right)_{\text{in effluent}} + \left( \text{Ethane formed from other feed components} \right)}{\left( \text{Ethane in feed} \right)} \quad (9)$$

where the units are in moles.

The yield of ethane measured in the reactor effluent is used to calculate the apparent conversion. Its definition is similar to that given in Eq. 9, but with the last term of the righthand side numerator eliminated.

The above definitions of conversions can be extended to all components present in the feedstock. The true conversion is always higher than or equal to the apparent conversion. The difficulty, however, always lies in estimating the third term in the righthand side numerator of Eq. 9.

In this study, the ethane yield from propane in admixture with ethane has been taken as identical to the ethane yield from propane as a pure feedstock. A similar approach is followed with the feeds containing butanes.

## Ethylene Yield

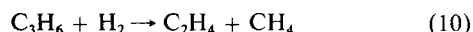
From the results of this experimental program, it is observed that the presence of hydrogen reduces the yields of propylene and other higher olefins due to hydrogenation. Also, the concentrations of allyl and methyl allyl radicals are reduced together with the inhibition effect discussed by Sundaram and Froment (1977). The above behavior is in direct competition with the reverse path of reaction 3, which results in an ethylene reduction. There is, however, a major difference between ethane pyrolysis and the cracking of mixtures containing ethane, propane, and butanes. In ethane cracking, the yield of liquid

products (C5+) is very small and the competing effect of the hydrogenation reaction described above is only minor. Thus, the ethylene is reduced.

In the case of the ethane, propane, and butane mixtures, the yield of liquid products is significant. In the presence of hydrogen, this liquid fraction is hydrogenated and then pyrolyzed, resulting in the production of additional ethylene. This competing path for the production of ethylene definitely overcomes the ethylene reduction resulting from the reverse path of reaction 3.

### Propylene Yield

Another important reaction is the radical analogue of the following molecular reaction,



In ethane cracking, the propylene yield is very low, approximately 1 wt. % of feed. However, in the mixtures of ethane/propane and ethane/propane/butanes, the propylene yield could be as high as 15 to 16 wt. % of feed. Therefore, in the presence of hydrogen, the propylene yield is reduced while the yields of ethylene and methane are enhanced according to reaction 10. The reduction in propylene yield is supported by the experimental data obtained in this study.

In conclusion, in the presence of hydrogen, the yields of olefins and diolefins are reduced due to hydrogenation and due to a decrease in the probability of the olefins formation. When the yields of C5+ fraction are appreciable, the hydrogenated products are further pyrolyzed, producing significant quantities of ethylene. In this case, the hydrogenation reaction path predominates over the reverse reaction 3, resulting in an overall ethylene yield enhancement.

### Notation

- $F_o$  = moles of ethane in feed, mol/h  
 $F_t$  = total molar flow rate =  $F_o(1 + X + \alpha + \beta)$ , mol/h  
 $K_p$  = equilibrium constant  
 $P$  = total system pressure, kPa  
 $P_{\text{C}_2\text{H}_4}$  = partial pressure of ethylene, kPa  
 $P_{\text{C}_2\text{H}_6}$  = partial pressure of ethane, kPa  
 $P_{\text{H}_2}$  = partial pressure of hydrogen  
 $T$  = temperature, °C or K

### Greek letters

- $\alpha$  = moles of hydrogen in feed/mol  $\text{C}_2\text{H}_6$  in feed  
 $\beta$  = moles of steam in feed/mol  $\text{C}_2\text{H}_6$  in feed  
 $\delta$  = dilution ratio, moles of hydrogen + moles of steam/mol  $\text{C}_2\text{H}_6$  in feed =  $(\alpha + \beta)$

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