Simultaneous Thermal Cracking and Oxidation of Propane to Propylene and Ethylene

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Propane conversion by its simultaneous endothermic thermal cracking and exothermic noncatalytic oxidative conversion to propylene and ethylene in the presence of steam and limited oxygen was investigated at various process conditions (temperature, 635–800°C; C_3H_8/O_2 ratio in feed, 2.0–16.0; H_2O/C_3H_8 ratio, 0.0–2.5; space velocity, 1,170–7,150 h^{-1}; and sulfur additive/C_3H_8 ratio, 10^{-3}–10^{-5}). Influence of a sulfur additive (thiophene, CS_2, or dimethyl sulfide) in the feed on process performance was also studied. The propylene/ethylene mole ratio in the products is decreased with increasing the temperature but increased with the C_3H_8/O_2 and H_2O/C_3H_8 ratios and space velocity. At all the process conditions, the selectivity for CO, a useful byproduct, is much more than that for CO_2. Because the thermal cracking of propane is carried out in the presence of limited O_2, not only the total conversion of propane but also the conversion of propane by its thermal cracking alone is increased greatly. Hence this process occurs at a much lower temperature or contact time than that required for achieving the same conversion in the thermal cracking process. Since the endothermic thermal cracking and exothermic oxidative conversion reactions of propane occur simultaneously, both reactions are coupled to make it highly energy-efficient, with a drastic reduction in external energy requirement and coke formation, and safe to operate. The overall process can be made almost thermoneutral, mildly exothermic, or mildly endothermic by manipulating the temperature and C_3H_8/O_2 ratio in the feed.

Introduction

Propylene, an important feed stock in the petrochemical industry, is produced along with ethylene (which is a main product) by the thermal cracking of ethane, ethane–propane mixture, or naphtha in the presence of steam (Kniel et al., 1980; Zdonik, 1983). Since the demand for propylene is increasing day by day, efforts are being made to develop processes for producing propylene from propane, particularly by catalytic oxidative dehydrogenation of propane (Chaar et al., 1988; Sam et al., 1990; Smits et al., 1991, 1995; Burch and Crabb, 1993; Corma et al., 1993a,b; Huff and Schmidt, 1994; Gao et al., 1994a,b; Yoon et al., 1994; Eon and Volta, 1994; Bharadwaj and Schmidt, 1995; Blasco et al., 1995; Mamedov and Corberan, 1995; Parmaliana et al., 1996; Watling et al., 1996; Lee et al., 1997). Propylene with high yields has also been obtained by the noncatalytic oxidative dehydrogenation of propane (Burch and Crabb, 1993).

Thermal cracking of propane occurs to an appreciable extent only at high temperatures (> 700°C) (Burch and Crabb, 1993). In this process, methane and ethylene are also formed as major products along with propylene. In general, hydrocarbon thermal cracking processes are highly endothermic and consume large amounts of energy and also involve extensive coke formation. The large amount of coke deposited on the inner walls of a tubular cracking reactor causes problems, such as reduced heat transfer from reactor walls, requiring a higher wall temperature (up to 1,100°C) and consequently requiring more energy. Because of this the life of the reactor tubes is reduced. There is also a need for process breakdown for physically removing the coke from the tubes from time to time.

It is of great practical importance to improve the performance of the propane thermal cracking process and also to reduce the energy requirement in the process. Our earlier studies (Choudhary and Mulla, 1997) indicated that the pro-

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cess performance and energy requirement in the thermal cracking of ethane to ethylene can be improved and most of the limitations of the thermal cracking process can be overcome by carrying out the ethane cracking in the presence of limited oxygen. Because of the presence of limited oxygen, both the exothermic oxidative conversion and endothermic thermal cracking of ethane occur simultaneously, making this process highly energy efficient, with a drastic reduction in external energy requirement and coke formation. Therefore, it is also interesting to study the thermal cracking of propane in the presence of limited oxygen.

The objectives of this investigation were to study in detail the thermal (noncatalytic) cracking of propane to propylene and ethylene in the presence of limited oxygen in order to avoid coke formation and to reduce the energy requirement in the process. The process was carried out in an empty quartz reactor at different temperatures, propane/O_2 and steam/propane ratios, and space velocities, using different sulfur compound additives in the feed.

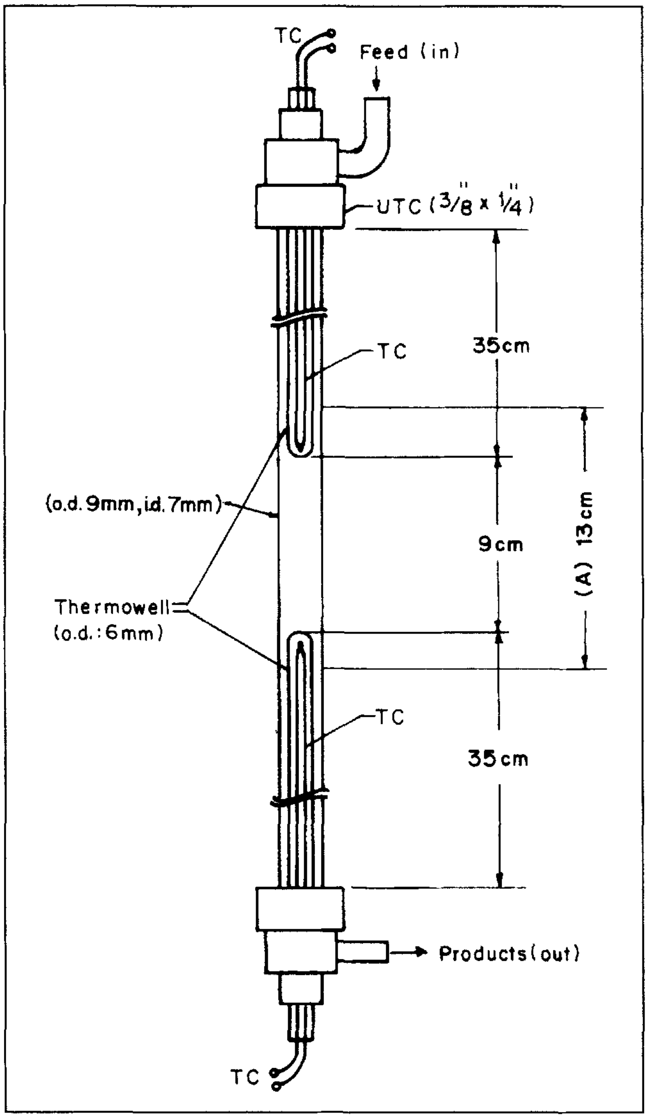

Figure 1. Quartz reactor used for the thermal and oxycracking of propane.

TC = thermocouple; UTC = ultra-torr connector; A = constant temperature zone of tubular electric furnace used for the reactor.

Experimental Section

The thermal propane cracking reactions were carried out in a continuous-flow quartz reactor, as shown in Figure 1. The reactor has a low dead volume. The reactor was kept in a tubular electric furnace such that the reaction zone was in the constant temperature zone of the furnace. The feed was a mixture of pure propane, steam, and the sulfur compound (viz., thiophene, CS_2, and dimethyl sulfide) with or without oxygen. The thermal cracking of propane in the presence of O_2 was carried out at different process conditions (temperature = 635–800°C; C_3H_8/O_2 ratio in feed = 2.0–16.0; H_2O/C_3H_8 ratio = 0.0–2.5; gas hourly space velocity (GHSV) = 1,170 – 7,150 h^{-1}; and sulfur compound additive/C_3H_8 ratio = 10^{-3}–10^{-5}). All the ratios of feed components are mole ratios. GHSV is defined as the volume of gaseous feed (measured at 0°C and 1 atm pressure) passed through a unit volume of the reactor per hour. The inlet and outlet temperatures of the reactor were measured by Chromel-Alumel thermocouples, as shown in Figure 1. The maximum difference in the reactor inlet and outlet temperatures was 7°C. The reactions were carried out by a procedure similar to that described earlier (Choudhary et al., 1991). After removal of water by condensation at 0°C, the feed and products were analyzed by an on-line gas chromatograph with a thermal conductivity detector (TCD) and flame ionization detector (FID), using Poropak-Q and Spherocarb columns. The water condensed from the products was weighed. The water formed in the reaction was obtained from the material balance.

The formation of O-containing products other than CO, CO_2, and H_2O was not observed. For obtaining oxygen balance, the amounts of free O_2, CO, CO_2 and H_2O present in the feed and products were taken into consideration. The experimental runs with the error in C, H, and O mass balances less than 6% were considered; the runs with higher errors were discarded.

Results and Discussion

Thermal cracking of propane in the absence of O_2

Results of the thermal cracking of propane at different temperatures in the absence of O_2 are shown in Figure 2. The propane conversion and product selectivity are strongly dependent upon the temperature, particularly above 700°C. At lower temperatures ($\leq$ 700°C), the conversion is very small ($<$ 7%) and the products formed are mainly methane and ethylene, with almost no formation of propylene. Above 700°C, the conversion and propylene selectivity increased markedly, and the selectivity for ethylene and methane decreased appreciably with increasing temperature.

At higher temperatures ($\geq$ 700°C), formation of coke on the reactor walls and/or a tarlike product (brownish/blackish thin layer deposited on the cooler parts of the reactor) is also observed in the thermal cracking of propane.

Enhancement in thermal cracking of propane by O_2

Results showing the influence at different concentrations (O_2/C_3H_8 mole ratio = 0–0.5) of the presence of O_2 in feed

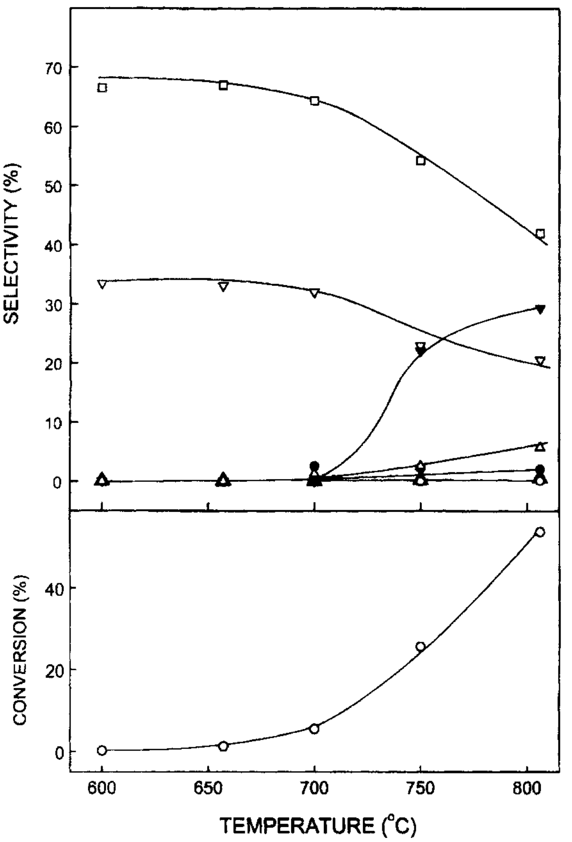

Figure 2. Influence of temperature on the thermal cracking of propane.

Feed = a mixture of propane, steam, and thiophene; $H_2O/C_3H_8 = 0.5$; thiophene/$C_3H_8 = 10^{-4}$; and GHSV = 3,000 h^{-1}. ▲—CO; ○—CO_2; ▽—CH_4; □—C_2H_4; ●—C_2H_6; ▼—C_3H_6; △—C_{4+}.

Table 1. Total Conversion of Propane and Its Conversion by Thermal Cracking in the Feed*

Temp. (°C)	Conc. of O_2 Rel. to C_3H_8	Propane Conv. (%)	
		Total	Thermal Cracking
635	0.00	0.8	0.8
	0.06	15.1	7.0
	0.13	23.4	6.3
	0.25	47.0	27.4
	0.50	72.0	42.4
660	0.00	1.6	1.6
	0.50	74.7	49.0
715	0.00	7.5	7.5
	0.50	74.7	56.6
800	0.00	53.9	53.9
	0.06	61.8	59.0
	0.13	68.6	62.2
	0.25	79.2	72.6
	0.50	91.7	77.4

*Steam/C_3H_8 and thiophene/C_3H_8 ratios in feed = 0.5 and 1×10^{-4}, respectively, and GHSV = 3000 h^{-1}.

on the total conversion of propane and its conversion purely by thermal cracking at different temperatures (635–800°C) are presented in Table 1. Because of the presence of O_2, not only the total conversion of propane but also its conversion purely by thermal cracking is much higher than that observed in the absence of O_2. Both the total conversion of propane and its conversion by thermal cracking alone are increased markedly by increasing the concentration of O_2 relative to propane at all the temperatures. However, the enhancement in the thermal cracking of propane is much higher at the lower temperatures ($\leq$ 660°C). The enhancement is decreased with increasing temperature and increased with increasing O_2 concentration relative to propane at all the temperatures. The observations could be explained by the free-radical chain initiation and propagation reactions occurring in the process in the presence and absence of O_2 as follows.

In the absence of O_2, propane is thermally activated only at higher temperatures (above 700°C), and its reaction is initiated through the scission of a C–C bond:

$$C_3H_8 \Leftrightarrow CH_3\cdot + C_2H_5\cdot \quad (1)$$

Since a C–H bond energy (99.8 kJ·mol^{-1}) is higher than a C–C bond energy (88.3 kJ·mol^{-1}), a break in C–H bond-forming propyl radicals is less probable. After the initiation of propane conversion (reaction 1), the formation of propyl radicals is expected to result from the attack on propane molecules by the methyl, ethyl, and hydrogen (formed in reactions 4 and 5) radicals:

$$C_3H_8 + C_2H_5\cdot(\text{or } CH_3\cdot \text{or } H\cdot) \Leftrightarrow C_3H_7\cdot + C_2H_6(\text{or } CH_4 \text{ or } H_2) \quad (2)$$

The propyl radicals are of two types: *n*-propyl radical ($1-C_3H_7\cdot$) and isopropyl ($2-C_3H_7\cdot$). These propyl and ethyl radicals undergo thermal decomposition (Falconer and Knox, 1959; Nguyen and Kung, 1991) as follows:

$$1-C_3H_7\cdot \Leftrightarrow C_2H_4 + CH_3\cdot \quad (3)$$

$$2-C_3H_7\cdot \Leftrightarrow C_3H_6 + H\cdot \quad (4)$$

$$C_2H_5\cdot \Leftrightarrow C_2H_4 + H\cdot \quad (5)$$

The hydrogen, methyl, ethyl, and propyl radicals undergo further complex free-radical chain propagation and termination reactions (Sundaram and Froment, 1978; Trimm and Turner, 1981; Dente and Ranzi, 1983), leading to the formation of different products (H_2, methane, higher alkanes, alkenes, and coke) in the propane cracking process.

However, in the presence of oxygen, propane is activated at lower temperatures (even at 635°C) and the chain initiation reaction is expected to occur through an abstraction of H from propane molecules by O_2, forming propyl radicals:

$$C_3H_8 + O_2 \Leftrightarrow C_3H_7\cdot + HO_2\cdot \quad (6)$$

Additional propyl radicals from propane are also formed by the following chain propagation:

$$C_3H_8 + HO_2\cdot \Leftrightarrow C_3H_7\cdot + H_2O_2 \quad (7)$$

$$H_2O_2 \Leftrightarrow 2OH\cdot \quad (8)$$

$$C_3H_8 + OH\cdot \Leftrightarrow C_3H_7\cdot + H_2O \quad (9)$$

The propyl radicals can also undergo reaction with O_2, forming propylene (Falconer and Knox, 1959):

$$C_3H_7\cdot + O_2 \Leftrightarrow C_3H_6 + HO_2\cdot \tag{10}$$

The ethyl radicals (formed simultaneously in reaction 1) may also undergo a reaction with O_2, forming ethylene:

$$C_2H_5\cdot + O_2 \Leftrightarrow C_2H_4 + HO_2\cdot \tag{11}$$

Thus, in the presence of limited O_2, propane is activated thermally (reaction 1) and by O_2 (reaction 6) and the preceding elementary pyrolytic and oxidation reactions, along with other possible chain-propagation and -termination reactions (including the H_2, CH_4, CO, CO_2, and H_2O forming reactions) that occur simultaneously. The relative importance of these reactions, however, depends on the temperature and O_2 concentration. The enhancement in thermal cracking of propane due to the presence of O_2 at all the temperatures is expected because of the formation of propyl radicals from propane by reactions 6–9 simultaneously with the elementary pyrolytic reaction (reaction 2).

At lower temperatures ($\leq 660°C$), the observed higher enhancement in the thermal cracking of propane is expected, mostly because of the formation of propyl radicals from propane by reactions 6–9, which is followed by the thermal decomposition of the propyl radicals by reactions 3 and 4, as well as by the subsequent propagation reactions promoted by the methyl and hydrogen radicals produced in the reactions. At higher temperatures ($\geq 715°C$), however, reaction 1 also becomes important, and hence enhancement, due to the presence of O_2, is less at the higher temperatures. This explanation is consistent with the observation that the conversion of propane purely by its thermal cracking (at 635–800°C) is increased by increasing the O_2 concentration; the increase is, however, smaller at the higher temperatures (see Table 1).

No coke or tarlike product formation was observed when the process was carried out in the presence of oxygen in the feed with a propane/O_2 mole ratio ≤ 16. This is probably because of the oxidation of coke precursors (highly reactive unsaturated hydrocarbons species) to carbon oxides. However, for the feed with a high propane/O_2 ratio (≥ 32), a brownish tarlike product formation at $\geq 750°C$ was observed.

The observed influence of oxygen in the feed on the thermal cracking of propane is quite similar to that observed earlier (Choudhary and Mulla, 1997) for the cracking of ethane in the presence of O_2. However, the enhancement in the rate of thermal cracking due to the presence of oxygen for the propane cracking is higher than that for the ethane cracking, particularly at higher temperatures.

Coupling of exothermic and endothermic reactions

Because of the simultaneous occurrence of all the previously cited free-radical reactions, there is a coupling of the exothermic oxidative conversion and endothermic thermal cracking reactions of propane in the presence of limited O_2. The main important exothermic and endothermic propane conversion reactions involved in the process are as follows.

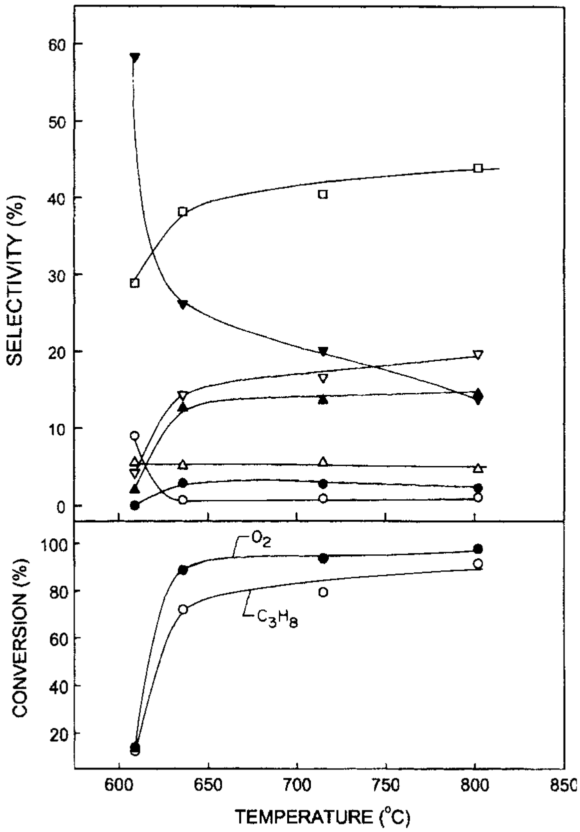

Figure 3. Influence of temperature on the oxycracking of propane.

$C_3H_8/O_2 = 2.0$; $H_2O/C_3H_8 = 0.5$; thiophene/$C_3H_8 = 10^{-4}$; and GHSV = 3,000 h^{-1}. ▲—CO; ○—CO_2; ▽—CH_4; □—C_2H_4; ●—C_2H_6; ▼—C_3H_6; △—C_{4+}.

Exothermic Reactions

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + 489.0\ \mathrm{kcal \cdot mol^{-1}} \quad \text{(at 700°C)} \tag{12}$$

$$C_3H_8 + 3.5O_2 \rightarrow 3CO + 4H_2O + 286.4\ \mathrm{kcal \cdot mol^{-1}} \quad \text{(at 700°C)} \tag{13}$$

$$C_3H_8 + 0.5O_2 \rightarrow C_3H_6 + H_2O + 28.3\ \mathrm{kcal \cdot mol^{-1}} \quad \text{(at 700°C)} \tag{14}$$

Endothermic Reactions

$$C_3H_8 \rightarrow C_2H_4 + CH_4 - 18.7\ \mathrm{kcal \cdot mol^{-1}} \quad \text{(at 700°C)} \tag{15}$$

$$C_3H_8 \rightarrow C_3H_6 + H_2 - 30.9\ \mathrm{kcal \cdot mol^{-1}} \quad \text{(at 700°C)} \tag{16}$$

Results showing the influence of process conditions on the conversion, product selectivity, and occurrence of thermal cracking of propane relative to its oxidative conversion (TC/OC reaction ratio) and also on the net heat of reaction (ΔH_r) are presented in Figures 3–9.

Results of the oxycracking of propane in the presence of different sulfur compound additives (viz., thiophene, CS_2, and dimethyl sulfide) are presented in Table 2.

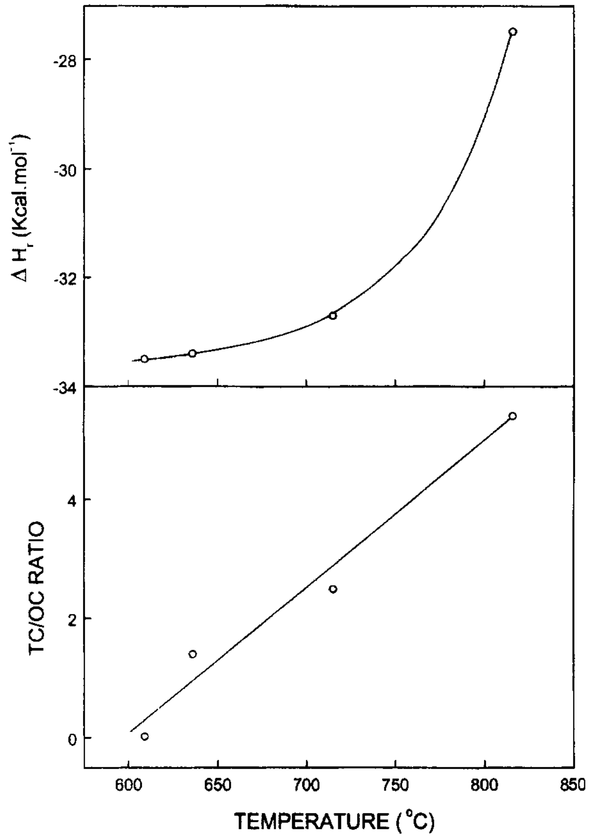

Figure 4. Influence of temperature on the TC/OC reaction ratio and net heat of reaction (ΔH_r) in oxycracking of propane.

$C_3H_8/O_2 = 2.0$; $H_2O/C_3H_8 = 0.5$; thiophene/$C_3H_8 = 10^{-4}$; GHSV = 3,000 h^{-1}.

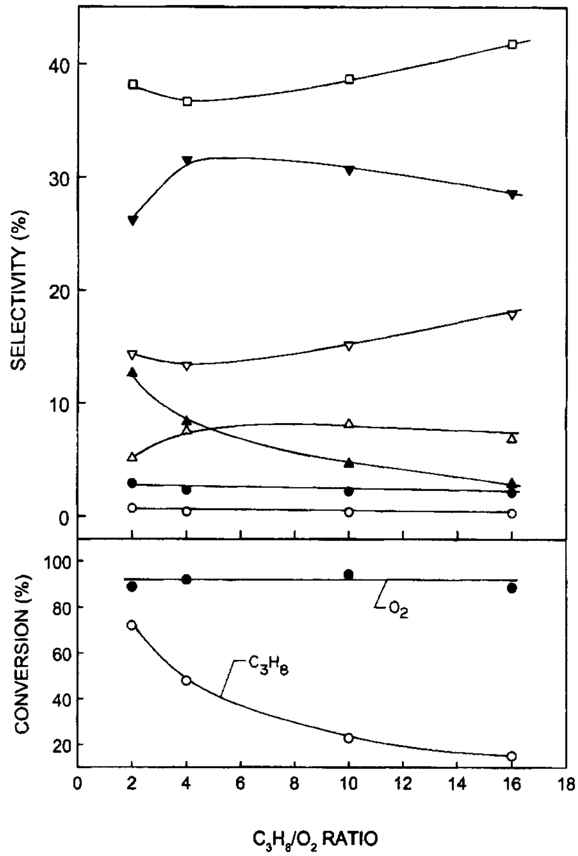

Figure 5. Influence of C_3H_8/O_2 on the oxycracking of propane at 635°C.

$H_2O/C_3H_8 = 0.5$; thiophene/$C_3H_8 = 10^{-4}$; GHSV = 3,000 h^{-1}. ▲—CO; ○—CO_2; ▽—CH_4; □—C_2H_4; ●—C_2H_6; ▼—C_3H_6; △—C_{4+}.

The net heat of reaction (ΔH_r, expressed in kcal per mole of propane converted) in the propane cracking process is obtained by subtracting the heat of formation (at the reaction temperature) of the components in the feed from that of the components present in the product stream. The overall process is exothermic and endothermic when the net heat of reaction (ΔH_r) is negative and positive, respectively. The oxygen (free O_2 or oxygen in CO, CO_2, and H_2O) balance between feed and products reveals that, among the exothermic reactions (reactions 12–14), the CO-forming reaction (reaction 13) is most predominant, and it occurs to a much larger extent than the other two exothermic reactions (reactions 12 and 14). Note that the oxidative dehydrogenation occurs to a much smaller extent than the CO_x-forming reactions.

Effect of process variables on conversion

The results show the following influence on the conversion. As expected, the conversion of both propane and O_2 is increased by increasing the temperature, the increase being very strong at lower temperatures (Figure 3). The conversion is, however, decreased by increasing the space velocity (Figure 9) and steam/C_3H_8 ratio (Figure 8), particularly at the higher space velocities and steam/C_3H_8 ratios, respectively. At the lower space velocities and steam/C_3H_8 ratios, the influence on the conversion is very small. The conversion of O_2 is not influenced significantly by a change in the C_3H_8/O_2 ratio (Figures 5 and 6). However, the propane conversion is very strongly affected by the C_3H_8/O_2 ratio; it decreased sharply when the C_3H_8/O_2 ratio was increased (Figures 5 and 6). As explained in an earlier section, the large increase seen in the propane conversion when the concentration of O_2 is increased relative to that of propane (Figures 5 and 6, Table 1) is not only because of the increased oxidative conversion of propane but also because of the increased enhancement in the thermal cracking of propane.

The results in Table 2 show that the propane conversion is increased due to the addition of thiophene, CS_2, or dimethyl sulfide (DMS) in the feed. The increase in the conversion due to the addition of thiophene or DMS is, however, higher.

Effect of process variables on selectivity

The influence of process variables on product selectivity (obtained on mole basis) is shown in Figures 3, 5, 6, 8, and 9 and Table 2. With the increase in the temperature, selectivity for propylene and CO_2 is decreased sharply, but that for ethylene, methane, CO, and ethane is increased; the selectivity for C_{4+} is almost unchanged (Figure 3). The influence of the C_3H_8/O_2 ratio on product selectivity is, except for propylene at the higher temperature (800°C) and for CO, relatively

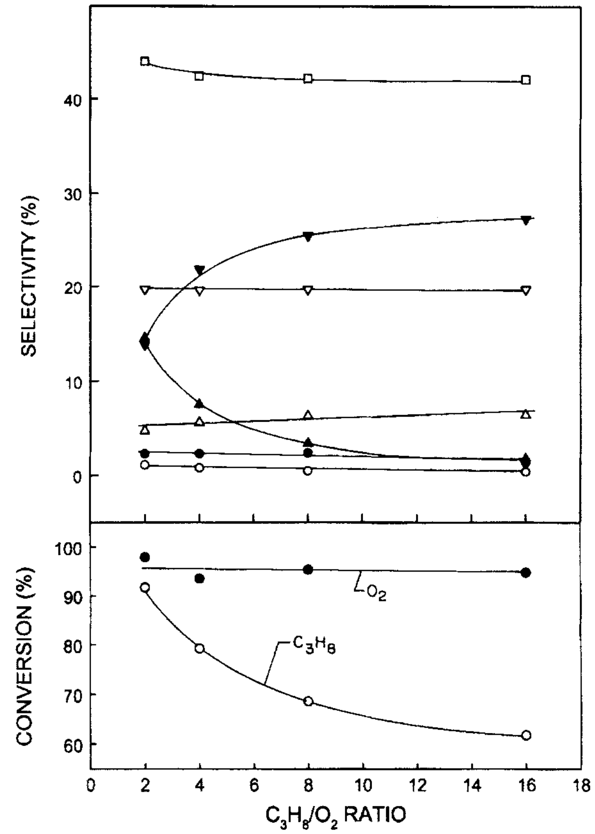

Figure 6. Influence of C_3H_8/O_2 on the oxycracking of propane at 800°C.

$H_2O/C_3H_8 = 0.5$; thiophene/$C_3H_8 = 10^{-4}$; GHSV = 3,000 h^{-1}. ▲—CO; ○—CO_2; ▽—CH_4; □—C_2H_4; ●—C_2H_6; ▼—C_3H_6; △—C_{4+}.

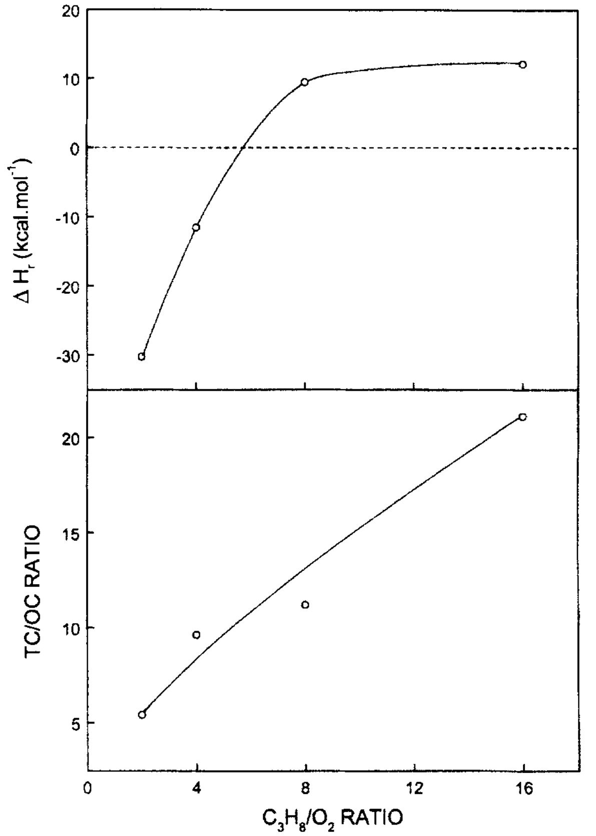

Figure 7. Influence of C_3H_8/O_2 on the TC/OC reaction ratio and net heat of reaction (ΔH_r) in oxycracking of propane at 800°C.

$H_2O/C_3H_8 = 0.5$ and GHSV = 3,000 h^{-1}.

small. CO selectivity is decreased and propylene selectivity (at 800°C) is increased by increasing the C_3H_8/O_2 ratio. The influence of the C_3H_8/O_2 ratio on the selectivity for propylene, ethylene, and methane is different at the two temperatures (635° and 800°C), indicating its strong dependence on the temperatures (Figures 5 and 6). The selectivity for propylene is increased and that for ethylene and methane is decreased by increasing the steam/C_3H_8 ratio (Figure 8) and space velocity, except at the lower space velocities (Figure 9). Among the sulfur compound additives (Table 2), thiophene with a thiophene/C_3H_8 ratio of 1×10^{-4} showed the highest selectivity for propylene and also for C_{2-4} olefins. On the other hand, because of the DMS additive, the propylene selectivity is decreased while the selectivity for ethylene, methane, and CO is increased. Further studies are necessary to understand the role of sulfur compound additives in the oxycracking process.

It may be noted that, at all the process conditions, the selectivity for CO (which is a useful byproduct) is much higher than that for CO_2.

Effect of process variables on the cracking/oxidation reaction ratio

The TC/OC reaction ratio, and consequently the ΔH_r in the process, are strongly influenced by the temperature and C_3H_8/O_2 ratio (Figures 4 and 7). The TC/OC ratio is increased and the heat produced in the process (or process exothermicity) is thereby decreased markedly by increasing the temperature and C_3H_8/O_2 ratio (or decreasing the concentration of O_2 relative to that of propane). The observed variation in the ΔH_r with the process variables is very consistent with that observed for the TC/OC reaction ratio. Thus, the net heat of all the propane conversion reactions, which occur simultaneously in the propane oxycracking process, can be controlled by manipulating the process conditions—viz, the temperature and concentration of O_2 relative to that of propane in the feed. The results (Figures 4 and 7) show that the process can be made mildly exothermic or mildly endothermic or even thermoneutral by manipulating the process conditions.

The preceding results reveal that, by carrying out the propane cracking process in the presence of limited O_2 (concentration of which is nowhere near the explosion limit), it is possible to convert propane into propylene and ethylene with high conversion and selectivity and also with a large energy saving. The maximum possible external energy saving would be equivalent to the heat of reaction of the thermal cracking of propane, which is an endothermic process. It can be seen that the amount of external energy required for the propane conversion reaction can be drastically reduced by making the reaction mildly endothermic, or this energy can be eliminated by making the reaction thermoneutral or mildly exothermic.

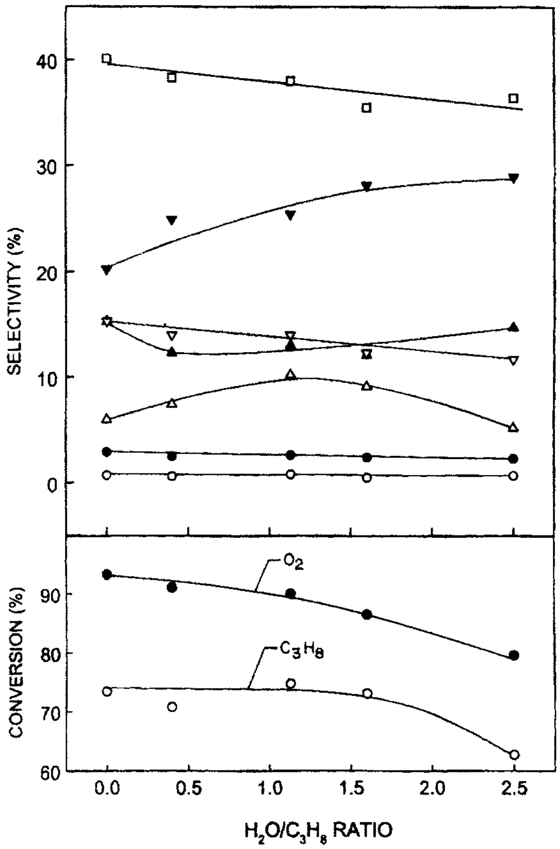

Figure 8. Influence of H_2O/C_3H_8 on the oxycracking of propane.

Temperature = 635°C; C_3H_8/O_2 = 2.0; thiophene/C_3H_8 = 10^{-4}; GHSV = 3,000 h^{-1}. ▲—CO; ○—CO_2; ▽—CH_4; □—C_2H_4; ●—C_2H_6; ▼—C_3H_6; △—C_{4+}.

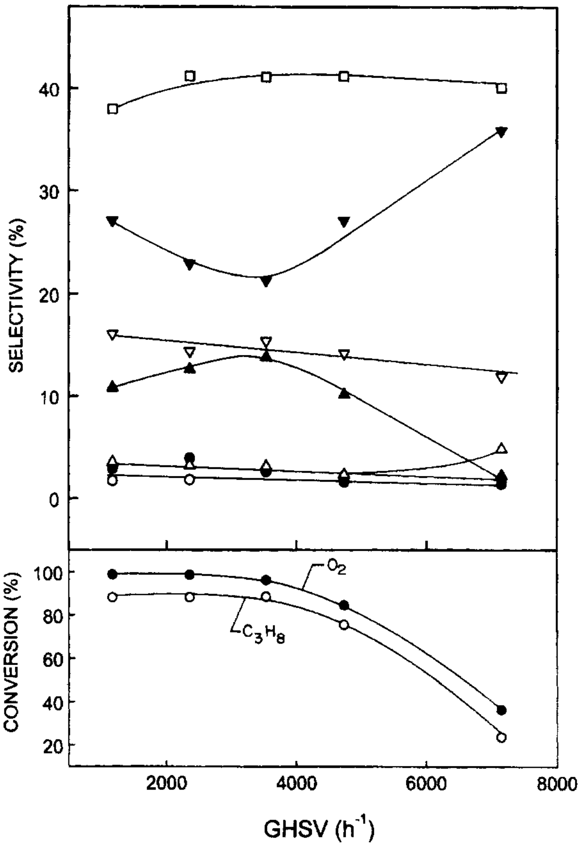

Figure 9. Influence of GHSV on the oxycracking of propane.

Temperature = 635°C; C_3H_8/O_2 = 2.0; thiophene/C_3H_8 = 10^{-4}; H_2O/C_3H_8 = 0.5. ▲—CO; ○—CO_2; ▽—CH_4; □—C_2H_4; ●—C_2H_6; ▼—C_3H_6; △—C_{4+}.

Further, since the heat produced in the exothermic reactions (reactions 12–14) is used instantly by the simultaneously occurring endothermic reactions (reactions 15 and 16), the overall process occurs in a highly energy efficient and safe manner without formation of hot spots, and hence also without risk of explosion.

It may be noted, however, that in the propane oxycracking process there is some carbon and hydrogen loss due to the formation of carbon oxides and water, respectively, in the propane oxidation reactions. Nonetheless, the reduced carbon selectivity is the price to be paid for gaining the advantages (lower coke formation, lower temperature, lower contact time or higher productivity, and less energy required) of the coupled process over the thermal cracking process. If the CO formed in this process is taken into consideration for utilization in CO-based processes, however, the process economics would be greater than in the cracking processes.

Effect of process variables on propylene/ethylene ratio

Results showing the influence of process conditions on the formation of propylene relative to that of ethylene in the process are presented in Figure 10. The propylene/ethylene ratio is decreased sharply by increasing the temperature, but it is increased by increasing the C_3H_8/O_2 and H_2O/C_3H_8 ratios and space velocity. However, the influence of the H_2O/propane ratio is less. Thus, the ratio shows a strong dependence on the propane conversion (Figures 3, 6, 8, and 9); it is decreased by increasing the conversion.

Table 2. Effect of Sulfur Additive in the Feed on the Conversion and Selectivity in the Oxycracking of Propane*

Sulfur Additives (A):	—	Thiophene			CS_2	DMS
A/C_3H_8 Ratio × 10^3:	0.0	0.01	0.1	1.0	0.1	0.1
Conversion (%)						
C_3H_8	70.8	76.2	77.1	75.7	71.1	78.6
O_2	91.1	91.4	91.9	91.0	92.3	91.1
Selectivity (%)						
CO	12.3	12.5	12.4	13.3	12.5	13.8
CO_2	0.6	0.6	0.7	0.6	0.6	0.7
CH_4	14.0	14.6	14.0	14.5	14.0	14.5
C_2H_4	38.3	39.4	38.2	38.8	38.2	40.1
C_2H_6	2.5	2.8	2.9	2.7	2.9	2.5
C_3H_6	24.9	23.8	26.2	23.6	25.2	21.6
C_4H_8	1.9	1.5	1.6	1.6	1.7	1.8
C_4H_{10}	5.5	4.8	4.0	4.9	5.0	5.0
C_{2-4} Olefins	65.1	64.7	68.2	64.0	65.1	63.5

*C_3H_8/O_2 = 2.0; temperature = 635°C; and GHSV = 3,000 h^{-1}.

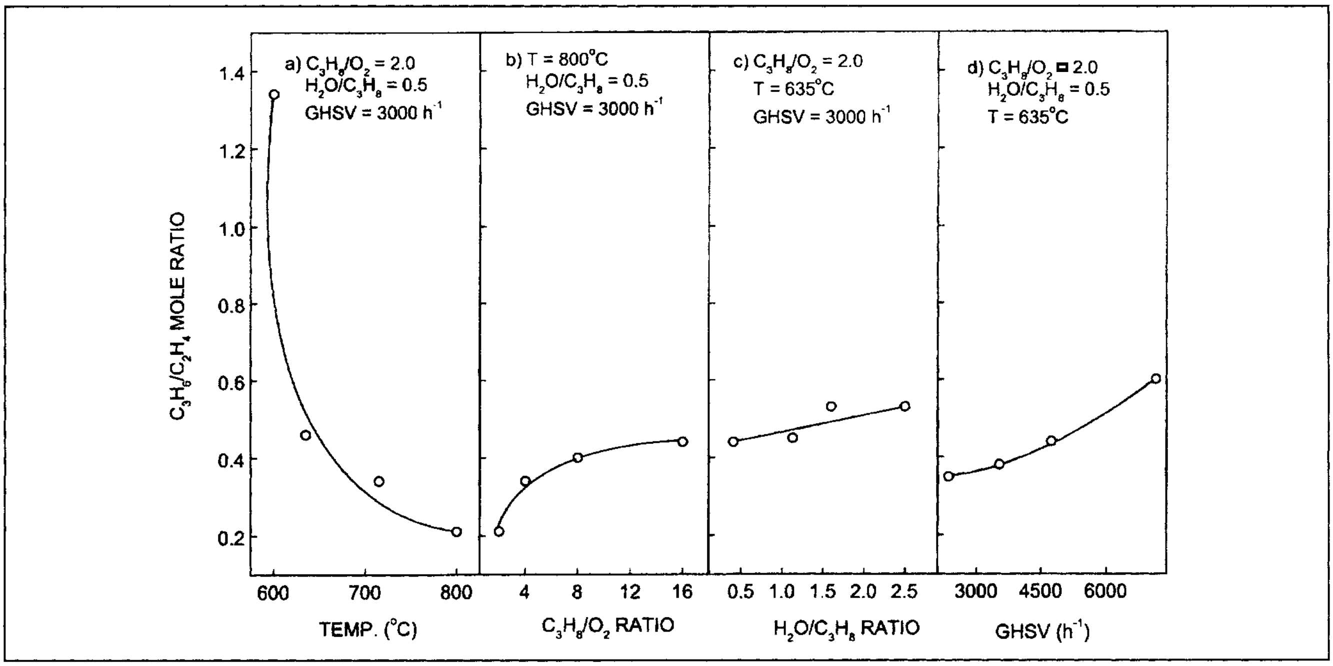

Figure 10. Influence of temperature, C_3H_8/O_2 and H_2O/C_3H_8 ratios, and space velocities on the propylene/ethylene ratio in the products (thiophene/$C_3H_8 = 10^{-4}$).

Conclusions

Adding limited O_2 in the feed of the noncatalytic propane cracking or pyrolysis process for producing propylene and ethylene has the following advantages over the conventional nonoxidative propane pyrolysis process:

1. Not only is the total conversion of propane enhanced, but so also is the conversion of propane purely by its thermal cracking. The oxycracking process therefore occurs at a much lower temperature or contact time than that required for the thermal cracking process to achieve the same converison.

2. The exothermic oxidative conversion and the endothermic thermal cracking reactions of propane occur simultaneously, making this process very energy efficient and safe by merging the exothermic and endothermic reactions, thereby drastically reducing the amount of external energy needed.

3. The formation of cokè and/or tarlike product is eliminated or drastically reduced.

4. The carbon loss due to CO_x formation is compensated for by the formation of CO over CO_2; the selection of CO (which is a useful byproduct) is much greater than CO_2 at all the process conditions.

The exothermicity or endothermicity of the process can be controlled by manipulating the temperature and O_2 concentration relative to propane in the feed. The addition of a sulfur compound, particularly thiophene, in the feed helps us attain a higher conversion of propane and also higher selectivity for propylene. The propylene/ethylene ratio in the products is strongly influenced by the process conditions, particularly the temperature, propane/O_2 ratio, and space velocity.

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