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Oxidative Pyrolysis of Ethane

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The effects of the addition of oxygen to the feed of an ethane steam cracker for ethylene production were investigated at industrial conditions by means of experiments and computer simulations. The oxidation of a small fraction of ethane feedstock in the cracking coil generates a significant amount of heat which can be used by the endothermic pyrolysis reactions. With this, the heat-transfer limitation in the industrial crackers is released. The addition of oxygen increases the conversion of ethane, while the yield to ethylene decreases slightly. Simulations indicate that the effects of the oxygen addition can be beneficial to industrial crackers in three manners: decreased residence time or increased throughput, higher severity, or reduced tubeskin temperature and longer coil lifetime.

Introduction

Ethylene is the most important bulk petrochemical. The steam cracking of ethane to ethylene is highly endothermic and is carried out at high temperatures in long coils which are heated in fired furnaces. The process gas is cracked at temperatures up to 1140 K. It is known that a short furnace residence time leads to improved olefin selectivity (Grantom and Royer, 1987). However, the lower residence time requires more intensive heat transfer to the process gas and increased furnace firing. Therefore, the throughput and severity of cracking is limited by the heat transfer through the coil.

For many years, intensive research has been conducted on alternative technologies for the production of ethylene. One promising route is the addition of oxygen to the hydrocarbon feedstocks. The exothermic reaction enthalpy of the oxidation reactions partly compensates for the endothermicity of the cracking reaction. The available literature on the oxidative cracking can be divided into three areas: the early work in noncatalytic oxidative cracking, the oxygen-aided cracking of heavy oil fractions, and the catalytic oxidative dehydrogenation of ethane to ethylene at lower temperatures.

The early work dates back from the 1940s and 1950s, when an oxygen content as high as 34% was used in the ethane cracker feed (Petroleum Processing, 1946; Deanesly, 1950). A single-pass ethylene molar selectivity of 80% was reached at an ethane conversion level of 50–60%.

The target of the oxygen-aided cracking of heavy oil fractions was to decrease the cost of raw materials and to secure the feedstock supply, particularly in the 1970s period after the oil crisis. Alternative feedstocks such as crude or residual oil were investigated. To achieve a sufficient heat supply, oxygen was added to the feedstocks and partial combustion of the feed took place. The advanced cracking reactor process represents a good example of this development. Ethylene yields as high as 34 wt % were reported. In addition, reactor types other than long coils were used, and solid heat carriers were applied. A more comprehensive review of this type

of unconventional processes can be found in *Hydrocarbon Processing* (Hu, 1982).

The catalytic oxydehydrogenation of ethane has also attracted continuous interest since the 1970s (McCain, 1982; Zhou et al., 1995). The goal is to operate at temperatures which are significantly lower than the present industrial operation conditions. Although this seems a valid possibility, it falls out of the scope of this study.

The aim of this work is to investigate the effects of the oxygen addition to the feed of industrial ethane crackers. The oxygen composition in the feedstock was maintained below 15 mol %, mostly around 5 mol %. In this way, a part of the heat, required by the endothermic pyrolysis, can be supplied in situ by combusting a fraction of the feed ethane. No attempt was made to operate the cracking autothermally, i.e., without external heat supply through the furnace, as was done in the earlier work (Deanesly, 1950). The effect of oxygen addition to an ethane cracking unit was also simulated. The discussion of the results is focused on the impact of the oxygen addition on the industrial ethane crackers.

Experimental Section

Equipment and Procedures. The experiments were carried out using gases with purities of 99.995% for N₂ and O₂ and 99.5% for ethane; steam was obtained from distilled water. The reactants were premixed before entering the empty tubular reactor. The reactor tubes used are manufactured from sintered dense α -aluminium oxide, corundum, or stainless steel (Incoloy 800) having an external diameter of 16.0 mm and an internal diameter of 8.0 mm. An α -aluminium oxide thermocouple well, having an external diameter of 4.0 mm and an internal diameter of 2.0 mm, was positioned along the reactor axis. The corundum reactor and thermocouple tubes were pretreated with a 60% HNO₃ solution for 1 h, followed by thorough washing with distilled water and subsequent heating in air at 1123 K. The Incoloy 800 tube was pretreated by contact with a mixture of 50% steam in helium for 20 h at 1123 K.

The reactor diameter, the reactor length, and the total flow rates were such that assumption of a plug flow regime is allowed (Cleland and Wilhelm, 1956). Since the highly turbulent flow regimes usually encountered

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Figure 1. Temperature vs axial reactor coordinate (corundum reactor). (+) $y_{\text{ox}} = 0\%$ (at $T_{\text{oven}} = 1314$ K) and (Δ) $y_{\text{ox}} = 15\%$ (at $T_{\text{oven}} = 1253$ K). $p_{\text{tot}} = 141$ kPa, $\tau = 0.2$ s, and $\delta = 0.3$.

in industrial reactors can also be described by plug flow, the experimental results can be directly compared with those to be expected in industrial reactors.

The reactor tube is surrounded by a fluidized silica bed which was heated by an oven. The axial temperature profile in the reactor was measured for every experiment, two examples are shown in Figure 1. The maximum temperature in the profile will be referred to as the reaction temperature T_{max} . The reactor pressure was maintained at 141 kPa (absolute pressure) by a back pressure regulator. The composition of the reactor effluent was analyzed by on-line gas chromatographic analysis; the C, H, and O balances were within 5–10%.

Definition and Calculation of Important Variables. The average residence time τ is calculated from $V_r p_{\text{tot}} / (F_{\text{tot}} RT_r)$. The effective reactor volume V_r is calculated from the internal and external reactor diameter and the reactor length, 0.265 m, which corresponds approximately to the length of the zone having a temperature higher than 973 K. Above this temperature, the thermal cracking reactions are initiated.

The conversion of ethane and oxygen is defined as the amount of reactant [kg s^{-1}] that has been converted divided by the amount of reactant [kg s^{-1}] in the feed. The product yield is defined as the amount of a specific product [kg s^{-1}] divided by the initial amount of reactant [kg s^{-1}]. The ethylene selectivity is defined as the amount of ethylene formed [kg s^{-1}] divided by the amount of ethane reacted [kg s^{-1}].

Results and Discussion

Experimental Conditions. The experimental conditions at which the initial tests were done were chosen as close as possible to the conditions industrially applied; this is a residence time of 0.1–0.4 s, a temperature of 1173 K, a total pressure of 141 kPa, and an ethane to steam ratio of 0.3 kg of $\text{C}_2\text{H}_6/\text{kg}$ of H_2O . For the oxidative pyrolysis experiments an initial molar oxygen content of 5 mol % was selected. All these conditions were varied to find the optimal conditions for comparing normal pyrolysis with oxidative pyrolysis.

1. Influence of Residence Time. The ethane conversion and the yield of ethylene and most other products show an increase with residence time, leveling off at residence times longer than 0.2 s. Due to the increase of the CH_4

Figure 2. Conversion, selectivity, and yield vs T_{max} (corundum reactor). $p_{\text{tot}} = 141$ kPa, $y_{\text{ox}} = 5\%$, $\tau = 0.2$ s, and $\delta = 0.3$.

Figure 3. Conversion, selectivity, and yield vs oxygen content (corundum reactor). $T_{\text{max}} = 1173$ K, $p_{\text{tot}} = 141$ kPa, $\tau = 0.2$ s, and $\delta = 0.3$.

yield, however, the ethylene selectivity decreases with increasing residence time. Hence, a residence time of 0.2 s was selected for the other experiments. The oxygen conversion was complete in all experiments.

2. Influence of Steam Dilution. Variation of the steam content δ between 0.2 and 0.5 kg of steam/kg of ethane did not significantly influence the performance in the corundum reactor. Slightly higher yields of methane, ethylene, and carbon monoxide were obtained at $\delta = 0.5$, the highest steam content investigated. A steam content of 0.3, which is commonly used in commercial ethane steam cracking, was chosen for the other experiments.

3. Influence of Temperature. Figure 2 shows that both the ethane conversion as well as the ethylene yield increase with reaction temperature. A higher reaction temperature also leads to significant increases of the yields of methane and acetylene, and to a less extent of the yields of carbon monoxide and propylene. Further, a small decrease of the yield of propane was observed. As the ethylene selectivity starts to decrease significantly at temperatures above 1173 K, a reaction temperature of 1173 K was selected for the investigation of the influence of oxygen addition to the feed.

4. Influence of Oxygen Content. Figure 3 shows the results of the influence of the oxygen content, y_{ox} , in the feed at fixed residence time, reactor temperature/pressure, and steam content. An increase of y_{ox} increases the ethane conversion and only slightly de-

creases the ethylene yield at a feed oxygen composition higher than 5 mol %. Nearly all the oxygen reacts to give CO which explains the proportional increase of the CO yield and the proportional decrease of the ethylene selectivity with y_{ox} . The slight decrease of the ethylene yield with increasing y_{ox} is accompanied by an increase of the methane yield. The yield of acetylene, propane, and propylene are hardly influenced by y_{ox} . Traces of CO₂ with yields up to a maximum of 0.3 wt % were found as well.

The reactor required less heating in order to achieve the same maximum temperature in the axial temperature profile when the oxygen content was increased. When y_{ox} was increased from 0 to 15 mol %, the setpoint of the oven temperature could be decreased by approximately 60 K. Figure 1 shows the effect of y_{ox} on the axial temperature profiles of the reactor; the addition of oxygen shifts the hottest zone slightly toward the reactor entrance.

5. Acetylene, Higher Hydrocarbons, and Oxygenates. The yield of acetylene was generally 1 wt % or less, except at the highest temperature investigated, 1273 K, at which the acetylene yield amounted to 3 wt %. The yield of propylene was about 1 wt % and did not significantly depend on residence time, temperature, and oxygen content. The yield of propane was in all experiments less than 0.5 wt %. The yields of propadiene and propyne were small and never exceeded 0.03 wt % for either of these compounds. Additional gas chromatographic analyses have shown the presence of small amounts of some higher hydrocarbons, especially butenes and in particular 1,3-butadiene and isobutene (up to a maximum of 2 wt %). The yields of C₅ products were between 0.1 and 0.5 wt %, and the yields to C₆⁺ components varied between 0.1 and 2 wt %. Generally, the amounts increased with increasing reaction temperature; however, these amounts did not depend on the amount of oxygen added. Oxygenates such as aldehydes, alcohols, and organic acids were not observed in any of the additional analyses performed.

6. Experiments in a Stainless Steel Reactor. An additional series of experiments was performed using an Incoloy 800 stainless steel reactor. The ethane conversion as well as the ethylene yield were found to be about 5% lower compared with those obtained in the corundum reactor. The yields of C₃⁺ products were lower; however, the stainless steel reactor walls caused an increase of the yield of carbon dioxide from approximately 0.05 to 1 wt % and a decrease of the carbon monoxide yield from approximately 3 to 2 wt %. Other trends which were observed for the corundum reactor were also observed with the stainless steel reactor. Further, there were no significant differences between the axial temperature profiles obtained with both reactors. The small differences observed between both reactors, however, justifies the use of the data obtained with the corundum reactor for a comparison with those obtained in an industrial reactor.

Computer Modeling. For modeling of the thermal cracking of ethane in the absence of oxygen, the computer model SPYRO is used (Barendregt et al., 1981). This model uses a reaction model on the basis of elementary reactions of the pyrolysis process.

The thermal energy is released by the partial combustion of ethane to CO, since the CO₂ amounts found experimentally were very small:

Table 1. Simulation of the Influence of the Oxygen Addition on Ethane Cracking Throughput

y_{ox} [mol %]	0	5
p_{inlet} [kPa]	1.98	2.19
p_{outlet} [kPa]	1.41	1.41
T_{outlet} [K]	1148	1148
τ [s]	0.153	0.141
$X_{\text{C}_2\text{H}_6}$ [%]	68.8	68.9
$Y_{\text{C}_2\text{H}_4}$ [wt %]	55.2	54.1
S [wt %]	80.2	78.4
relative ethylene production [kg h ⁻¹]	1	1.14

The standard reaction enthalpy of this reaction amounts to -2.89×10^4 kJ/kg_{C₂H₆}, which will be absorbed by the process gas. When 5% oxygen is cofed to the coil, this corresponds to 12–16% of the total heat input necessary for the thermal cracking, depending on coil geometry, residence time, and temperature.

Since the model is not designed to simulate combustion reactions, a few assumptions and simplifications were necessary to simulate oxidative pyrolysis. Because it was experimentally found that the addition of oxygen did not significantly influence the selectivity to any of the products except carbon monoxide and water, the incorporation of the effect of the addition of oxygen was mainly the heat effect of the oxidation. The effect of the additional dilution by the oxygen in the feed and the products CO and H₂O formed from this were taken into account in the simulation.

Further, it was assumed that the heat generated by the oxygen consumption was homogeneously generated in the entire coil. Although in reality the rate of oxygen consumption is likely to be higher in the beginning of the reactor than at the end of the reactor, the assumption is justified by the small difference between the axial temperature profiles obtained experimentally with and without oxygen addition, as shown in Figure 1. If the oxidation would take place only in a short zone near the entrance of the reactor, the curve corresponding to 15% O₂ should already drop below the curve corresponding to 0% O₂ in the first part of the reactor. The fact that this was not found experimentally indicates that the oxidation reaction takes place in a broad zone of the reactor. The heat generated by the combustion reactions was incorporated by assuming a higher maximum heat flux to the process gas inside the cracking coil than what a state-of-the-art steam cracking furnace can supply, i.e., 1.16×10^2 kW m⁻². Since the heat production by the oxidation amounts to 12–16% of the heat consumption of the cracking process without oxygen addition, a 14% higher maximum heat flux was used: 1.32×10^2 kW m⁻².

1. Simulations. In industrial practice, the in situ generated heat can be utilized in three ways. First, the throughput of the reactor can be increased, or the residence time can be lowered at the same throughput, since there is an additional amount of heat available to the process gas. Secondly, keeping the throughput the same, the severity of cracking, e.g., the conversion of ethane, can be increased. Finally, when keeping throughput and severity the same, the maximum tube temperature can be lowered since the required heat flux is decreased due to in situ heat generation; this will result in longer cycle times and a cracking coil lifetime. The effect of each of these ways was investigated by performing simulations.

2. Oxidative Pyrolysis with Higher Throughput. Table 1 shows the influence of 5 mol % oxygen addition on the throughput; the inlet and outlet temperature of the

Table 2. Simulation of the Influence of the Oxygen Addition on Ethane Cracking Severity

y_{ox} [wt %]	0	5
T_{outlet} [K]	1148	1173
p_{outlet} [kPa]	1.41	1.41
τ [s]	0.153	0.153
$X_{\text{C}_2\text{H}_6}$ [%]	68.8	80.9
$Y_{\text{C}_2\text{H}_4}$ [wt %]	55.2	60.4
S [wt %]	80.2	74.7

Table 3. Simulation of the Influence of the Oxygen Addition on Tubeskin Temperature

y_{ox} [mol %]	0	5
T_{outlet} [K]	1148	1148
p_{outlet} [kPa]	1.41	1.41
τ [s]	0.153	0.153
$X_{\text{C}_2\text{H}_6}$ [%]	68.8	70.8
$Y_{\text{C}_2\text{H}_4}$ [wt %]	55.2	55.2
S [wt %]	80.2	78.0
tubeskin temperature [K]		
coke free	1332	1313

cracking coil and the ethane conversion have been set equal in both simulations by choosing the appropriate pressure and residence time. The total throughput of the coil can be increased at the expense of only a slight loss of selectivity. The 14% increase of the ethylene production is equal to the relative increase of the heat flux. These results show the possibility of increasing the ethylene production in an industrial cracking coil by the addition of oxygen because heat transfer limitations are released.

3. Oxidative Pyrolysis at High Severity. Table 2 shows the results of the simulations related to the high severity of the oxidative pyrolysis. By the addition of oxygen, the coil outlet temperature is increased from 1146 to 1173 K. The single-pass conversion is increased from 68.8 to 80.9 wt %, which is very high in comparison with the 60–65% severity at which most industrial ethane crackers operate and the highest reported severity used, 70%. The ethylene yield increases from 55.2 to 60.4 wt %. Due to the partial oxidation of ethylene, however, the selectivity to ethylene decreases from 80.2 to 74.7 wt %.

These results show the possibility to booster the single-pass ethane conversion by 10–20% and the ethylene yield by more than 5% in an industrial cracking coil. With this, the production of ethylene per pass is raised, at a small expense of a decrease in the ethylene selectivity, however.

4. Lower Tubeskin Temperatures by Oxidative Pyrolysis. The addition of oxygen can also be used for lowering the tubeskin temperature, which results in longer operation cycle times and a longer coil lifetime. Table 3 shows the effect of 5 mol % oxygen addition on the tubeskin temperature. The oxygen addition leads to a reduction of the tubeskin temperature of about 20 K at the start of an operation cycle. This temperature difference increases with the operation time because the lower tubeskin temperature leads to lower coking rates. This means that with 5 mol % oxygen addition the operation cycle time can be increased by at least 20 days in an industrial cracking coil. This leads to a longer cracking coil lifetime.

Conclusions

The effects of adding oxygen to the feed of an ethane steam cracker have been investigated both experimentally and with computer simulations. The experiments

showed that the addition of oxygen increases the ethane conversion. The ethylene yields decrease slightly at the feed oxygen compositions higher than 5 mol %, which is the result of a slight decrease in ethylene selectivity. The oxygen is nearly completely converted to CO, but generally speaking, the oxygen addition does not have a drastic influence on the product distribution.

The computer simulations showed that the oxygen addition has a large impact on the heat effect of the cracking reaction. The heat effect can be beneficial to the industrial cracker operations in three different manners. The residence time can be lowered which can be translated to an increase in throughput. The severity of ethane cracking can be further increased; as high as an 80 % single-pass ethane conversion is achievable with addition of 5 mol % oxygen. Alternatively, the tubeskin temperatures can be lowered, which can be translated to an extended operation cycle time and coil lifetime.

Notation

F_{tot} = total molar flow [mol s⁻¹]

p_{tot} = total pressure [Pa]

p = coil pressure [Pa]

R = gas constant [J mol⁻¹ K⁻¹]

S_j = selectivity of product j [%]

T_r = reactor temperature [K]

T = coil temperature [K]

V_r = reactor volume [m³]

X_i = conversion of reactant i [%]

Y_j = yield of product j [%]

y_{ox} = molar percentage of oxygen in the feed (on dry basis) [mol %]

δ = steam/ethane ratio [kg of steam/kg of ethane]

τ = average residence time [s]

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