TPO-GC AND TG-DTA INVESTIGATION OF DRY DECOKEING PROCESS IN OLEFIN PLANTS

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Abstract

The aim of this work is to investigate the combustion mechanism of catalytic coke formed in the olefin plants furnaces as a chemical reaction fouling. The objectives are removing the steam injection and modeling a dry oxidation process based upon Thermogravimetry (TG) and Temperature-Programmed Oxidation-Gas Chromatography (TPO-GC) experiments. Comprehensive data were obtained for 5.0-15.0 % vol. oxygen content in the combustion atmosphere while the temperature was tuned from 600 to more than 1000°C. The concentrations of carbon monoxide and carbon dioxide were determined as TPO criteria for reaction rate and kinetic parameters along with the mass loss in TG tests. The results revealed the optimum decoking temperature in order to decrease the decoking run-time, improve energy conservation and enhance the cleaning efficiency. DTG thermogram revealed the temperatures that the combustion rate of catalytic coke increased gradually. TPO-GC experiments approved the optimal decoking temperature in accordance with the plant’s operation manual. The propounded dry decoking mechanism depicted the combustion reaction of carbon and CO\textsubscript{2} follows by O\textsubscript{2} chemisorption at carbon surface, obtaining the activation energy, converting to the activated complex and production of CO\textsubscript{2}.

Keywords: Combustion; Coke; Oxidation; Pyrolysis; Furnace; Modeling, Parametric Study.

1. Introduction

Steam cracking of hydrocarbons is one important process of the petrochemical industry for olefin production. Carbon deposition phenomena or coke formation deposit on the inner wall of coils is carbonaceous material that results of undesirable side reactions in steam cracking process and a major concern that limits run the length of the furnace in ethylene plants [1-2].

There is a numerous investigation on the mechanisms of carbon deposition under various conditions [1-12]. Generally, there are three categories of coke formation are as the following:

a. Catalytic coke with the filamentous structure of carbonaceous deposition as shown in Figure 1 is results of heterogeneous reaction where occur on the metal surface’s active sites (Cr, Ni, Co) and generally doing main role in radiant coil coking in furnaces [1-2, 10, 13].

b. Pyrolytic or gas phase coke deposition occurs by a radical mechanism where procurators joint with existing carbon layer and due to the growth of coke.

c. Coke formation by condensation mechanism is amorphous structure and happens in the low temperature sections [1, 3, 14].

Coke is poor heat conductor, and due to reducing heat transfer rate from flue gas to process gas in coils, increase pressure drop by growing coke layer and reducing cross section of coil, lower ethylene yield and heat input increased if the feed conversion maintained constant then coil skin temperature, gradually increased until reaches design temperature of reactor tube and finally cause to shut-down the furnace for coke removing during burning-off carbonaceous deposition via controlled combustion where carried out by means of a steam/air mixture [1, 3, 12-13].
The amount of coke accumulation depends on feed characteristics, operating severity, the material of coil, run length and the addition of inhibitors \cite{10,12}.

There are two alternative industrial decoking technologies exist currently for coke removal that difference of them is end points of decoke effluent. Effluent can be sent to decoke drum or injecting to from bottom or either to the lower end walls of firebox by symmetrical piping configuration for keep particle emissions below 50 mg/Nm³ during decoke which the second one applied in modern furnaces \cite{16}. Optimization of decoke operation is one of the main interests from the point of view of energy consumption and time of production loss reduction in olefin plants; therefore, it is necessary to determine the mechanisms of coke combustion reactions by real-time analyzing of the deposited coke produced in industrial plants \cite{6}.

Coke combustion is assigned as a de-volatilization process followed by the combustion of residual coke \cite{17-19} along with the side reaction of gasification \cite{20-22}. The combustion behavior of fine \cite{23} and coarse \cite{24-27} coal particles in the N₂/O₂ atmosphere was studied, and a model was propounded based on devolatilized products and heat-mass transfer phenomena was propounded. In the process of combustion, the carbon atoms in the coke structure react with surrounded oxygen from the point of weak bonds as depicted in Figure 2.

![Figure 1. Catalytic coke formation mechanism](image1)

There are many investigations reported by different researchers on various carbonaceous materials gasification and combustion like coal, coal char, coke, petcoke, sewage sludge char \cite{36-61}, biomass \cite{62-73}, coal-biomass blends \cite{74-75} and municipal solid wastes \cite{76-78}. Some of

![Figure 2. Graphical implementation of coke decomposition in combustion phenomena](image2)
the alternative reaction kinetics used by different workers illustrated in Table 1 and there are excellent reviews available which can consider on gasification and combustion of coal and chars [22, 79-85], carbon based deposits [86], municipal solid waste [87] and carbonaceous adsorbsents [88-89] and Biomass [90-95].

Table 1. Various reaction mechanisms for carbonaceous material gasification and combustion kinetics by various researchers

<table>
<thead>
<tr>
<th>Authors</th>
<th>Type of carbonaceous material</th>
<th>Weight (g)</th>
<th>Reaction model</th>
<th>Exp. instrument</th>
<th>T, °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jelemensky et al.</td>
<td>Coal char</td>
<td>0.002-0.003</td>
<td>[ C + O_2 \rightarrow CO_2 ] [ C + CO_2 \rightarrow 2CO ] [ C + O_2 \rightarrow CO ] [ CO + 0.5O_2 \rightarrow CO_2 ] [ C + 0.5O_2 \rightarrow CO ]</td>
<td>TG</td>
<td>amb.-800</td>
<td>[96]</td>
</tr>
<tr>
<td>Keskitalo et al.</td>
<td>Coke of a Ferri-elite Catalyst</td>
<td>0.01</td>
<td>[ C + 0.5O_2 \rightarrow CO ] [ C + O_2 \rightarrow CO_2 ] [ CO + 0.5O_2 \rightarrow CO_2 ]</td>
<td>TPO-GC</td>
<td>amb.-850</td>
<td>[97]</td>
</tr>
<tr>
<td>Gil et al.</td>
<td>Coal and pine sawdust</td>
<td>0.05</td>
<td>[ A (solid) \rightarrow B (char) + C (gas) ] [ B (char) \rightarrow C (gas) + D (ash) ]</td>
<td>TG- DTG</td>
<td>amb.-615</td>
<td>[98]</td>
</tr>
<tr>
<td>Micco et al.</td>
<td>Coal</td>
<td>0.10,0.16,0.30</td>
<td>[ C(g) + CO_2 \rightarrow 2CO(g) ]</td>
<td>drop tube furnace (DTF)</td>
<td>825-920</td>
<td>[99]</td>
</tr>
<tr>
<td>Nakasaka et al.</td>
<td>Coked MFI-type zeolite</td>
<td>0.1</td>
<td>[ C(g) + 0.5O_2 \rightarrow CO(g) ] [ C(g) + O_2 \rightarrow CO_2(g) ] [ H + 0.25O_2 \rightarrow 0.5H_2O ]</td>
<td>fixed-bed flow reactor, TG</td>
<td>550-650</td>
<td>[100]</td>
</tr>
<tr>
<td>Li et al.</td>
<td>Coal</td>
<td>0.005</td>
<td>[ C + CO_2 \rightarrow CO ]</td>
<td>TPO-TG</td>
<td>amb.-1450</td>
<td>[101]</td>
</tr>
<tr>
<td>Mandapat et al.</td>
<td>Coal char</td>
<td>0.01</td>
<td>[ C + CO_2 \rightarrow C(O) + CO ] [ C(O) + CO \rightarrow C + CO_2 ]</td>
<td>TG</td>
<td>amb.-1000</td>
<td>[102]</td>
</tr>
<tr>
<td>Zhang and et al.</td>
<td>Coal</td>
<td>0.1</td>
<td>[ C + O_2 \rightarrow C + O_2 ] [ C(g) + 2O_2 \rightarrow CO_2(g) ] [ X \rightarrow X ] [ X \rightarrow O_2 ]</td>
<td>TGA</td>
<td>&gt;200</td>
<td>[103]</td>
</tr>
<tr>
<td>Jing et al.</td>
<td>Coal</td>
<td>0.005</td>
<td>[ C + CO_2 \rightarrow 2CO ] [ C + CO \rightarrow C + CO_2 ]</td>
<td>TG</td>
<td>amb.-1300</td>
<td>[104]</td>
</tr>
<tr>
<td>Veca et al.</td>
<td>Coal char</td>
<td>0.2-0.3</td>
<td>[ C + CO_2 \rightarrow 2CO ]</td>
<td>TGA</td>
<td>800-1100</td>
<td>[105]</td>
</tr>
<tr>
<td>Urych</td>
<td>Coal</td>
<td>0.2-0.3</td>
<td>[ Coal \rightarrow x (volatiles) + (1 - x) (char) ] [ x \rightarrow ] [ the fraction of volatiles ]</td>
<td>TGA/DSC</td>
<td>298-1173</td>
<td>[106]</td>
</tr>
<tr>
<td>Veca &amp; Adrover</td>
<td>Coal char</td>
<td>0.02-0.03</td>
<td>[ C + CO_2 \rightarrow 2CO ]</td>
<td>TG</td>
<td>800-1000</td>
<td>[105]</td>
</tr>
<tr>
<td>Nunes et al.</td>
<td>Coal</td>
<td>0.03</td>
<td>[ C + O_2 \rightarrow C(O) ] [ C(O) \rightarrow CO ]</td>
<td>drop tube furnace (DTF)-TG</td>
<td>1100-1400</td>
<td>[108]</td>
</tr>
<tr>
<td>Ding et al.</td>
<td>Coal char and petroleum coke char</td>
<td>0.008</td>
<td>[ C + H_2O \rightarrow CO + H_2 ] [ CO + H_2O \rightarrow CO_2 + H_2 ] [ C + O_2 \rightarrow 2CO ]</td>
<td>drop tube furnace (DTF)-TG</td>
<td>1100-1400</td>
<td>[108]</td>
</tr>
<tr>
<td>Chen et al.</td>
<td>Coal</td>
<td>0.3</td>
<td>[ C + CO_2 \rightarrow C(O) ] [ C(O) \rightarrow CO + C ] [ C + H_2O \rightarrow H_2 + C(O) ] [ C(O) \rightarrow CO + C ]</td>
<td>drop tube furnace (DTF)-TG</td>
<td>1100-1400</td>
<td>[108]</td>
</tr>
<tr>
<td>Tanner et al.</td>
<td>Coal</td>
<td>0.01-0.015</td>
<td>[ C + CO_2 \rightarrow CO + H_2 ]</td>
<td>drop tube furnace (DTF)-TG</td>
<td>600-1100</td>
<td>[110]</td>
</tr>
<tr>
<td>Czerski et al.</td>
<td>Coal</td>
<td>0.46</td>
<td>[ C + CO_2 \rightarrow 2CO ]</td>
<td>TG</td>
<td>Amb-1100</td>
<td>[111]</td>
</tr>
<tr>
<td>Liu et al.</td>
<td>coal char</td>
<td>0.5</td>
<td>[ C + CO_2 \rightarrow 2CO ] [ C(O) \rightarrow CO + CO ]</td>
<td>TG</td>
<td>1050</td>
<td>[112]</td>
</tr>
</tbody>
</table>

The coke removal with decoking process reported in six heterogeneous and homogeneous reactions by Y. Zhang et al. [113] as Eqs. 1-6: 
\[ C(g) + O_2(g) \rightarrow CO_2(g) \] (1)
Heynderickx et al. [14] assumed coke is burning off phenomena undergoing with two fundamental endothermic gasification and oxidation reactions mechanism (Eq.1) and (Eq.2). In this study investigation was undertaken involving dry oxidation, therefore, reactions (Eq.2) and (Eq.6) is discarded. Boudouard reaction (Eq.5) ignored in addition because the ratio of CO to CO$_2$ decrease with increasing temperature and carbon monoxide convert to carbon dioxide rapidly. Finally, the set of reactions reduced to Eqs. 1, 3, 4 that enthalpies of formation at 298K respectively are as the following [113-115].

\[
\Delta H_{R1} = -394 \text{ kJ/mol} \\
\Delta H_{R3} = -110 \text{ kJ/mol} \\
\Delta H_{R4} = -284 \text{ kJ/mol}
\]

This work aimed to study the combustion characteristics of catalytic coke formed in the furnaces of an olefin plant which extract from a real piece of the coked coil that showed in Figure 3. For this purpose, the coke samples were combusted in a fixed bed tubular reactor under different O$_2$/N$_2$ atmospheres from 600 to 1000°C, and coke characters were identified by TG/DTG (Thermogravimetry/Differential Thermogravimetry) analysis and the TPO-GC experiments were conducted under non-isothermal conditions at controlled O$_2$/N$_2$ rates.

Figure 3. The cross-section of a piece of the radiant coil with inner wall coke deposit

The main objective was the development of a combustion model for nonporous catalytic coke based upon the weight percent of oxygen.

2. Experimental method
2.1. Materials and chemicals

Coke samples used in experiments were obtained from a piece of radiation coil of an ethane cracker furnace as shown in Figure 3 where were milled in the size of 1-2 mm and Table 2 illustrated the components of this coke.

<table>
<thead>
<tr>
<th>Test name</th>
<th>Test Method</th>
<th>Percent wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>ASTM D3174-11</td>
<td>0.8</td>
</tr>
<tr>
<td>Volatile</td>
<td>ASTM D3175-11</td>
<td>0.5</td>
</tr>
<tr>
<td>Fixed C</td>
<td>ASTM D3172-89(02)</td>
<td>98.4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>ASTM E1915-09</td>
<td>0.1</td>
</tr>
</tbody>
</table>

2.2. Experimental set-up

A horizontal cylindrical reactor with accessory equipment was heated in a digital furnace in the temperature range of 600-1000°C. The reactor was fed by air and nitrogen gasses while
the gas flows were determined and controlled by mass-flow meters (Brooks, 5850S, USA) in the range of 10 to 100 mL/min. The reactor tube was manufactured by a thermal resistant metal alloy (SS-304) with a diameter of 15 mm and a length of 200 mm, and experiments were carried out with coke samples located in a reactor tube. The sides of the reactor tube were blinded two four-neck flanges after the coke loading. The temperatures of the furnace, representing the reactor temperature and the flow of inlet gas streams were recorded by a PC system. The effluent gas was analyzed by gas chromatography equipped along with the released gas stream. Figure 4 shows the schematic of the experimental setup.

![Figure 4. Schematic of TPO-GC setup](image)

Gas chromatography runs were performed by a gas chromatograph (CP3800, Varian, USA) and He carrier gas (BOC, CP grade). The runs were carried out on 1.0 cm$^3$ fluent gas from the furnace in splitless mode, injector-temperature of 150°C and pressure of 15.0 psi. The packed column consisted of HAYESEP Q (80-100 mesh) with dimensions of 2 m x 1/8 inch OD x 2.0 mm internal diameters. The column temperature was set at 30°C for 4 min. The TCD filament temperature was set at 200°C.

The coke characteristics were determined by thermogravimetry (TG) analyzer (209F1, Netszch, Germany) to obtain TG and DTG traces of the pyrolytic coke samples. The atmosphere was set on ambient air, and the flow rate was fixed on 25 mL/min. The sample weight was selected to be 50-100 mg heated in the range of 30-900°C by the ramp of 20°C/min in an alumina-pan. Data was compiled and processed by Proteus Analysis Software.

### 2.3. Characteristic tests

The samples of catalytic coke, which accurately were weighted to 100 mg, were dried at 100°C for 20 min, then it was heated at a constant rate (ramp) of 20°C/min from 100°C to 600°C under air atmosphere (100 mL/min), then held at 1000°C for 10 min to complete devolatilization step. After that, the air stream (100 mL/min) was injected and the temperature decreased to ambient.

### 2.4. Combustion procedure

The TPO experimental setup, which has been depicted schematically in Figure 4, was a tubular reactor located in the thermostatically-controlled furnace. The reactor was loaded by 190, 138 and 501 mg of catalytic coke samples for combustion studies. The reason why the small quantity of coke was used is to ensure the exothermicity combustion reactions and the endothermicity cracking reactions do not fluctuate the temperature of the reactor bed. The temperature was increased from the ambient conditions to 600°C (20°C/min), from 600°C to 800°C (10°C/min), from 800°C to 1000°C (5°C/min) and held at 1000°C for 10 min. The temperatures were monitored by thermocouples placed around the reactor, and the pressure was fixed by pressure regulators at the outlet stream to the combustion-reactor. Along with the
reaction, the effluent gas stream passed through a sampling valve of gas chromatography resulted in the online determination of concentrations of carbon monoxide and carbon dioxide products. After the experiments, the residual coke in the reactor was flushed-out with nitrogen (100 mL/min) until 100°C. These residues were collected and weighted by analytical balance (Kern, Germany). The weight losses of residue samples of runs 1-3 were determined, and the results are depicted in Table 3.

Table 3. The weight loss of residue samples of runs 1-3

<table>
<thead>
<tr>
<th>Run</th>
<th>Primary weight (mg)</th>
<th>Secondary weight (mg)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>190</td>
<td>80</td>
<td>58</td>
</tr>
<tr>
<td>2</td>
<td>138</td>
<td>70</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>501</td>
<td>230</td>
<td>54</td>
</tr>
</tbody>
</table>

3. Results and discussions

3.1. TG Experimental results

TG experiment at air atmosphere was conducted, and the results are presented in Figure 5.

The combustion started at 700°C, and its rate was maximized at 900°C leading to a 30% decrease in the mass of the coke. The nonporous structure of catalytic coke shows a smooth line in the temperatures less than 700°C since no trapped or adsorbed hydrocarbons and water were released, and no mass-loss was recorded. DTG curve highlighted that from 700°C to 900°C the combustion rate increases gradually.

Figure 6 drew regarding TG data and Arrhenius relationship and mass basis rate of combustion formula:

\[
r_c = -\frac{1}{m} \frac{dm}{dt}
\]  

(10)

Slope changes at nick point in this figure indicate how the mechanisms controlled the rate of combustion. At the lower temperatures than 638°C the controlling mechanism is kinetic control, and at the higher temperatures than 638°C diffusion is controlling step which frequency coefficient and activation energies in these steps are 5.5847e+28, 167571.4 s⁻¹ and 237330, 59197 J.mol⁻¹, respectively and finally, rates of combustion in these mechanisms defined as the following Eqs. while \( R = 8.314 \text{ J/mol.K} \).

\[
r_c = 5.58 \times 10^{28} \exp \left(\frac{-237330}{RT}\right)
\]  

(11)

\[
r_c = 167571.4 \exp \left(\frac{-59197}{RT}\right)
\]  

(12)
3.2. Combustion mechanism of decoking

As discussed before, the combustion phenomena of catalytic coke were assessed experimentally under an oxygen atmosphere (5.0, 10.0 and 15.0 % vol.) and at different temperatures (600-1000°C) as their results presented in Table 4.

Table 4. Characteristics of experimental runs

<table>
<thead>
<tr>
<th>Run</th>
<th>Oxygen (% Vol.)</th>
<th>Time (min)</th>
<th>T (°C)</th>
<th>CO2 (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0</td>
<td>600</td>
<td>0.1953</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>700</td>
<td>0.1683</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>800</td>
<td>0.0782</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>850</td>
<td>0.7680</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>900</td>
<td>0.1547</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>950</td>
<td>0.3920</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>1000</td>
<td>0.2419</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0</td>
<td>600</td>
<td>0.1359</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>700</td>
<td>0.1121</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>800</td>
<td>0.1170</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27</td>
<td>835</td>
<td>0.1731</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>850</td>
<td>0.1318</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>900</td>
<td>0.1062</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>950</td>
<td>1.0883</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>1000</td>
<td>0.3389</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>1010</td>
<td>0.1192</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>0</td>
<td>600</td>
<td>0.0873</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>700</td>
<td>0.0704</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>800</td>
<td>0.2393</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27</td>
<td>835</td>
<td>0.0852</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>850</td>
<td>2.2566</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>900</td>
<td>0.2957</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>950</td>
<td>0.6548</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>1000</td>
<td>0.2700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>1010</td>
<td>0.1517</td>
</tr>
</tbody>
</table>

It is clearly obvious that the oxygen chemisorptions more in temperatures lower than 850°C in 1 and 3 runs and at the lower than 950°C in step 2 as seen in Table 4 and rapid CO2 formed desorption in 850°C and 950°C at 1, 3 and 2 runs, respectively occur due to oxygen chemisorbed before. The experimental results depicted that the maximum CO2 concentration was determined at 850°C in with 5 and 15 vol.% of oxygen concentrations media and at 950°C in respect to 10 vol.% which are in accordance with the field data for gas-feed olefin furnaces.

According to the results of Table 4, by increasing the temperature along with time, the concentration of produced CO2 is changed because of the revolution of surface phenomena including adsorption of O2 at carbon surface, formation of activated complexes of C–C–O, breaking the C–C bonds and release of CO2. The results of Table 4 were graphically implemented in Figure 7 to explain the decoking process based on the released concentration of CO2.

The main concentrations of the released CO2 are attributed to two temperatures of 850 and 950°C. The areas behind the traces, which reveal the overall production of CO2 along with temperature rise, represent that CO2 production at O2 concentration of 15% vol. was twice than that of for both O2 concentrations of 5 or 15% vol. Moreover, it is obvious that combustion reactions are conducted at two temperature regions of 800-900°C and 900-1000°C, with a quench temperature of Q~900°C in which the decoking reactions are assigned to be quenched.

The orders of CO2 production at two decoking regions of 800-900°C and 900-1000°C are not identical because of different decoking mechanisms.

In the region of 800-900°C, the magnitude of CO2 production follows as O2 concentrations of 10% < 5% << 15%. On the other hand, in the region of 900-1000°C, that magnitude follows as 5% < 15% < 10% vol. O2.
A combustion mechanism was propounded based upon the supposed reactions, which are assigned to occur in these conditions, and the results were matched with the experimental data gathered from TPO tests. Eqs. 1, 3 and 4 were proposed as the mechanism of these reactions as the following:

$$\text{C(s) + O}_2(g) \xrightarrow{k_1} \text{CO}_2(g)$$

(13)

$$\text{C(s) + 0.5O}_2(g) \xrightarrow{k_2} \text{CO(g)}$$

(14)

$$\text{CO(g) + 0.5O}_2(g) \xrightarrow{k_3} \text{CO}_2(g)$$

(15)

Respect to Eqs. 13, 14 and 15 and with the assumption of elementary reactions, the reaction rate of CO$_2$ ($r_{CO_2}$) production is determined as Eq. 16.

$$r_{CO_2} = k_1 C_{O_2} - k_-1 C_{CO} + k_3 C_{CO}, \frac{C_{O_2}^{1/2}}{2} - k_-3 C_{CO_2}$$

where: $k_1$, $k_-1$, $k_2$, $k_3$, and $k_-3$ represent the rate constants of reactions Eqs 13, 14 and 15, respectively. $C_{O_2}$, $C_{CO}$, and $C_{CO_2}$ show the concentration of oxygen, carbon monoxide and carbon dioxide gases as %wt.

Due to this fact that CO is intermediate; therefore, the concentration gradient with respect to time is assumed to be zero. Hence, according to the steady state hypothesis, the rate of CO reactions and its concentration is determined by Eqs. 17 and 18, respectively.

$$+ r_{CO} = k_-2 C_{CO}^2 - k_-3 C_{CO} - k_-3 C_{CO}, \frac{C_{O_2}^{1/2}}{2} + k_-3 C_{CO_2} = 0$$

(17)

$$C_{CO} = \frac{k_-2 C_{CO}^2 + k_-3 C_{CO}_2}{k_-2 + k_3 C_{O_2}^{1/2}}$$

(18)

In addition, GC reports revealed that the concentration of CO is determined to be negligible in the reaction atmosphere.

By replacing Eq. 18 in Eq. 16 and simplification, Eq. 19 is obtained.

$$-r_{CO_2} = \left[\frac{(k_1 k_-2 + k_2 k_3) C_{O_2} + k_1 k_3 C_{O_2}^{3/2}}{k_-2 + k_3 C_{O_2}^{1/2}}\right] - \left[\frac{k_-2 k_-3 + k_2 k_3 C_{O_2}^{3/2} + k_3 k_-3}{k_-2 + k_3 C_{O_2}^{1/2}}\right] C_{CO_2}$$

(19)
According to the above-listed \( k \) values, Eqs. 20 and 21 are given.

\[
\begin{align*}
\frac{k_3}{k_2} \gg k_{1-2} & \quad \text{(20)} \\
\frac{k_2}{k_3} \ll k_{1/2} \quad & \text{(21)}
\end{align*}
\]

Therefore, in the first assumption of this developed model, the \( k_{1-2} \) is negligible with respect to the \( k_{2/3} \) of Eq. 19 and it can be neglected. Likewise, in the second assumption of the model, the \( k_{1-2} \) and \( k_{2-3} \) are negligible with respect to the left term \( (k_{1-2} k_{3-1} C_{O_2}^{1/2}) \) of Eq. 19. Therefore, the rate of reaction (Eq. 19) is written as Eq. 22.

\[
r_{CO_2} = (k_2 C_{O_2}^{1/2} + k_1 C_{O_2}) - k_{-2} C_{CO_2}
\]

The developed model reveals that the overall rate constant is a function of the concentrations of oxygen and carbon dioxide. Therefore, it is possible to determine the overall rate constant of combustion reaction using the concentrations of oxygen and carbon dioxide in the combustion atmosphere.

The experimental data obtained from the combustion of catalytic coke and they were fitted to Eq. 22 in order to assess the accuracy of the proposed mechanism (Table 4).

The graphical illustration of the experimental data is depicted in Figure 7 representing a positive reaction rate when the \( CO_2 \) concentration increases and vice versa. Therefore, the bi-functional Eq. 22 is used to admit the variation of reaction signs.

The positive reaction rate at the increased \( CO_2 \) concentration is attributed to high concentration of \( O_2 \) in the combustion reaction leading to increasing the first term of Eq. 22, means moving to more positive values. On the other hand, when the \( CO_2 \) concentration decreases, the reaction rate moves to the negative values since the reaction of carbon to \( CO_2 \) follows by adsorption of \( O_2 \) at carbon surface, obtaining the activation energy, converting to the activated complex and production of \( CO_2 \).

Therefore, at descending concentration of \( CO_2 \), the carbon surface is going to adsorb \( O_2 \) and cannot react to it since the concentration of activated complex is low. At these conditions, the first term of Eq. 22 is reduced with respect to the second term, and the overall sign is negative.

The above discussions and the trend of Figure 8 were in accordance with three oxygen concentrations (5, 10 and 15% vol.) of combustion atmosphere, approving the proposed mechanism.
4. Conclusions

Dry oxidation of deposited catalytic coke on the coil surfaces of an ethane cracker furnace was studied by TG/DTA, and TPO-GC techniques and the main conclusions were drawn are

1- Arrhenius diagram analysis showed a change in controlling steps of combustion rate occurs at around 640°C (break point).
2- DTG thermogram revealed that in the range of 700-900°C the combustion rate of catalytic coke increased gradually. The maximum combustion rate was determined by TPO-GC experiments to be at 850°C, which is in accordance with the plant’s operation manual.
3- The positive reaction rate at the increased CO₂ concentration is attributed to high concentration of O₂ in the combustion reaction leading to moving the reaction rate to more positive values.
4- The proposed mechanism depicted that the combustion reaction of carbon and CO₂ follows by chemisorption of oxygen at carbon surface, obtaining the activation energy, converting to the activated complex and production of CO₂.
5- At the concentration of 5% and 15 % vol. oxygen and lower temperatures than 850°C, the rate of O₂ chemisorption is higher, and the rate of carbon monoxide formation is more in 850°C, and it similarly occurs for the concentration of 10 % vol, at 950°C. It is demonstrated that burning off coke in decoking of steam cracker furnaces is optimized by TG/DTA and TPO TPO-GC techniques usage leading to more energy conservation.

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References


