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Decomposition of VOCs in a continuous high-voltage pulsed corona process

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Abstract
To decompose VOCs (volatile organic compounds) in an air stream several new technologies are emerging. We are using a corona reactor for decomposing these VOCs. The advantage of our pulsed corona process is the energy efficiency with which the VOCs decompose. To examine the reactor, a model is developed which can describe the conversion of the VOCs in our industrial prototype high-voltage pulsed corona reactor.

Introduction
Volatile organic compounds (VOC) emission in air has to be reduced due to speculations about the environmental impact of these organic compounds in the atmosphere. For a new technology to be successfully offered for commercial use, it must be reliable, economically competitive and ready for use on an industrial scale [1]. Our pulsed corona reactor is approaching these prerequisites. It can remove several VOCs in dilute concentrations of 1-2500 ppm in air streams at atmospheric pressure in a continuous process. Pulsed high-voltage power generates an intense corona. The power source and reactor operate reliably and do not cause any EM interference to other apparatus.

In comparison with thermal oxidation reactions the decomposition of the VOCs by pulsed corona is more favorable because of the high energy efficiency. The reason of this efficiency is that in thermal oxidation processes, all the molecules of the gas are heated uniformly to a temperature at which the VOCs burn [1]. When pulsed corona energy is used for activating the oxidation reaction the energy is directed preferentially toward the decomposition of the VOCs. The heating of carrier gas molecules is negligible.

Experimental setup
Pulsed corona is generated by repetitive (1000/s) 100kV, 200ns wide pulses. The peak value of the corona current is 500 A. The peak pulsed power is 50MW. Excellent electromagnetic compatibility (EMC) between source and surrounding equipment has been achieved. The pulse source has an overall efficiency (mains-AC to corona power) of approximately 60%. The design of the source includes resonant pulse charging circuits, pulse transformers and a sparkgap switch. It is described in [2]. The VOCs that are used in the experiments are presented with their inlet concentrations in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Inlet concentration (ppm)</th>
<th>Mass flow VOC (g/h)</th>
<th>Corona power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>30-190</td>
<td>15.87</td>
<td>250-2540</td>
</tr>
<tr>
<td>Pentane</td>
<td>80-1000</td>
<td>6.73</td>
<td>138-1037</td>
</tr>
<tr>
<td>Toluene</td>
<td>125-450</td>
<td>18.40</td>
<td>137-1159</td>
</tr>
<tr>
<td>NO/Ethylene</td>
<td>213/30</td>
<td>6.5/1-23/2.7</td>
<td>153-1101</td>
</tr>
<tr>
<td>Ethylene</td>
<td>150-2500</td>
<td>17.14</td>
<td>184-1234</td>
</tr>
<tr>
<td>Propane</td>
<td>10-500</td>
<td>1.7-36</td>
<td>156-1149</td>
</tr>
<tr>
<td>Butane</td>
<td>50-2000</td>
<td>9.111</td>
<td>139-1193</td>
</tr>
<tr>
<td>TCA</td>
<td>80-1000</td>
<td>4.25</td>
<td>128-1127</td>
</tr>
</tbody>
</table>

TCA=1,1,1-trichloroethane

The choice for these VOCs is made in cooperation with the industry. The setup of the pulsed corona reactor for decomposition of VOCs is illustrated in Fig. 1.
Two reactors, with a length of 3 meters each and a diameter of 250 mm, are placed in series via a flexible aluminum-tube of about 2.5 meters length. A pump downstream the second reactor causes a flow from the surrounding air through the system at the flow rate of 21-109 m³/h. Due to this pump a small reduced pressure will exist in the system. The airflow can further be controlled by the use of high-pressure air at the inlet of reactor 1. Only the first reactor was operated with pulsed corona.

At the entrance of reactor 1 the air is mixed with the VOC. A mass flow controller doses the gases' ethylene, propane, butane or NO. Toluene, pentane, styrene and 1,1,1-trichloroethane are dosed by evaporating these VOCs. The saturated vapor is lead to reactor 1. In the center of reactor 1, an electrode is placed which is made from a wire with a diameter of 1 mm. The wall of the tubular reactor is covered with needles which are placed 15 mm above the wall. The pulsed corona operating conditions for reactor 1 are: a pulse repetition rate up to 1.5 kHz and a pulsed corona power up to 1.44 kW average.

At the end of reactor 2 we have a sample line to a gas chromatograph (GC). It is a capillary with a length of 4 m and an inside diameter of 1 mm. The GC (Hewlett Packard) analyses the composition of the gas quantitatively with a FID (flame ionization detector) and a poropak Q column or a SE54 column. The reactor is covered with needles which are placed 15 mm above the wall. The pulsed corona operating conditions for reactor 1 are: a pulse repetition rate up to 1.5 kHz and a pulsed corona power up to 1.44 kW average.

Thermodynamic properties
The VOC in the air is broken down in the tubular reactor through a chemical reaction. With a chemical reaction we are usually concerned with two features [3]: the extent to which it takes place and the rate of reaction. By the extent of the reaction we mean how completely the reactants convert to products after equilibrium has established. By the rate of the reaction we mean how rapidly the reactants are converted to products.

\[ A + B \rightleftharpoons \text{C} \]

The extent to which a reaction takes place can be expressed by an equilibrium constant Keq \((k_1/k_2)\). The equilibrium constant Keq is related to the change in the standard free energy for the reaction \(\Delta G^\circ\):

\[
\Delta G^\circ = -2,303RT \log \text{Keq}
\]

A large negative value of \(\Delta G^\circ\) (\(\Delta G^\circ < -12 \text{ kJ/mol}\)) will ensure that the reactants will completely convert to products after equilibrium is reached. When a reaction is capable to produce several products, the major product will be the one for which the value \(\Delta G^\circ\) is most favorable (most negative). In our case \(\Delta G^\circ\) only depends on the difference in bond energies between the reactants and the products.

In the following example reaction we explain how the reaction rate can be influenced by corona in the tubular reactor.

\[
\text{VOC} + \text{air} \xrightarrow{\text{Corona}} (\text{VOC} + \text{air})^* \rightarrow \text{P}
\]

We assume hypothetically that the mixture reached a higher energy state by adding or removing electrons to or from the mixture. When we assume a negative free energy change of the reaction, the product P of the reaction is at a lower free energy level as the reactants are. However, if covalent bonds are broken in a reaction, the reactants must go up an energy hill first, before they go downhill. We can present this graphically by plotting the free energy of the reactants against the reaction coordinate.

The transition state \((\text{VOC} + \text{air})^*\) can be reached by using corona energy. We are concerned about the activation energy, \(\Delta G^\ast\), needed for the decomposition of VOCs in the mixture. When we can predict this activation energy we also know the reaction rate constant. For the rate constant we can write:

\[
k = k_0 e^{(-\Delta G^\ast/RT)}
\]

In this equation \(k_0\) is the absolute rate constant, which equals the rate at which all transition states proceed to products. The level of the transition state depends on the chemical bond strength, in the mixture VOC and air, which have to be broken for reaction to the product P. These bonds have to be broken directly or indirectly by the energy of the electrons in the reactor. So when the electrons add a sufficient amount of energy, the transition state can be reached and reaction can occur.
Reactor design
The reactions are activated by use of corona energy in an oxidating environment. Since we do not know the mechanism for the reaction we must present an alternate expression for the reaction rate. The type of our corona reactor can be calculated out of the Pe number. With the experimental data we can find Pecllet numbers \((Pe = uL/D)\) of \(10^5 - 10^6\) which means we are dealing with a plug flow reactor [4]. In our tubular plug flow reactor we have Reynolds numbers of \(2000 - 10^4\) which means that the flow is turbulent. With this knowledge we can make a model for the conversion in the reactor. For this model we will make a mass balance over a small volume part of the reactor with length \(dz\). We make the following assumptions for the derivation of this model:
1. To decompose a VOC molecule in the mixture only electrical energy is used for activating the mixture.
2. The activation energy is independent of the VOC inlet concentration.
3. In the reactor we have a steady state situation.
4. The reactor is an ideal plug flow reactor.
5. The reaction is a first order reaction.

In our situation a first order reaction means that the reaction rate \(R\) is linear dependent on the VOC concentration. A mass balance for the VOC reads as:

\[
\frac{d(V_{\text{VOC}})}{dt} = \dot{F}_{\text{VOC}}(C_{\text{VOC}} - C_{(\text{VOC})_{\text{out}}}) - R_{\text{VOC}} dV
\]

With:
- \(R = \frac{(E/V_{\text{tot}})/\Delta G'_{\text{mix}})}{f}\)
- \(E = \text{corona power (J/s)}\)
- \(R = \text{reaction rate (mol/m}^3\text{s)}\)
- \(S = \text{specific power (kWh/kg}_{\text{VOC}}\)
- \(F_{\text{VOC}} = \text{VOC mass flow at the inlet of the reactor (g}_{\text{VOC}}/\text{h})\)
- \(\Delta G'_{\text{mix}} = \text{activation energy for the mixture: air+VOC (J/mol}_{\text{in}}\)
- \(f = \text{fraction VOC (mol}_{\text{VOC}}/\text{mol}_{\text{in}}\)
- \(V = \text{volume reactor (m}^3)\)
- \(C_{\text{VOC}} = \text{concentration VOC (mol/m}^3)\)
- \(t = \text{time (s)}\)
- \(F_{\text{V}} = \text{volume flow (m}^3/\text{s})\)
- \(\tau = \text{residence time (s)}\)

and with the boundary conditions:
- \(z = 0 \quad f = f_0\)
- \(z = L \quad f = f_l\)

For a pseudo-stationary state \((dC/dt = 0)\) eq.3, with the boundary conditions, leads to an expression for the conversion \((X=1-f_{\text{in}}):\)

\[
\frac{SF_{\text{VOC}}}{\Delta G'_{\text{mix}}v_{\text{VOC}}f_{\infty}} \cdot X = 1 - e^{-\frac{\Delta G'_{\text{mix}}v_{\text{VOC}}f_{\infty}}{\Delta G'_{\text{mix}}v_{\text{VOC}}f_{\infty}}}
\]

The total concentration (total gas density) \(C_{\text{tot}} (\text{mol}_{\text{tot}}/\text{m}^3)\) in the reactor can be calculated with the ideal gas law.

With this equation we can describe the experimental data, where the conversion \((X)\) is plotted versus the specific power \(S\). The fit parameter is the activation energy \(\Delta G'_{\text{mix}}\) of the mixture.

Experimental results
The results of the measurements are shown in Fig. 2. The plots in Fig. 2 are a summary of all experimental results for various residence times, inlet mass flows and values of corona power.

With styrene experiments we could detect intermediates. These intermediates were only detected during low corona power. The composition of the gas mixture was: styrene, benzaldehyde, benzene-acetaldehyde and 3-methylphenyl-1-ethanone. With higher corona power the intermediates disappeared.

With the other VOCs we did not detect intermediates. Our corona reactor decomposes the VOCs probably into stable oxidated products. We can make this conclusion because the products are not detected with the flame ionization detector of the GC which is based on burning (oxidating) the analyzed compounds.
Fig. 3 plots the calculated conversion (with eq.4) versus the measured conversion (removed fraction) for Toluene.

**Figure 3:** Comparison of the calculated conversion (eq. 4) and the measured conversion for Toluene.

**Discussion**

**Decomposition of the VOCs**

Styrene, toluene, ethylene and NO-ethylene mixtures can be decomposed completely with our pulsed corona reactor. The VOCs: butane, pentane, propane and 1,1,1-trichloro-ethane are not completely decomposed. The ethylene decomposition in the mixture NO-ethylene is influenced by NO. By making a comparison between the ethylene conversion and the NO-ethylene conversion (Fig. 2) we can recognize that ethylene can be decomposed after NO has disappeared. As we can see from the molar specific power $S_m$ data in Table 2, the compounds styrene, ethylene and NO are very efficiently decomposed. The NO is probably oxidized due to the production of oxygen radicals or the more stable ozone molecules.

**Table 2:** Specific power at X=63% and a specific $t$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S$ (kWh/kg$_{kmol}$)</th>
<th>$M$ (kg/kmol)</th>
<th>$S_m$ (kWh/kg$_{kmol}$)</th>
<th>$\Delta G^\circ_{max}$ (J/mol$_{kmol}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>7</td>
<td>104.16</td>
<td>729</td>
<td>255</td>
</tr>
<tr>
<td>Ethylene</td>
<td>12</td>
<td>28</td>
<td>348</td>
<td>922</td>
</tr>
<tr>
<td>NO</td>
<td>15</td>
<td>30</td>
<td>450</td>
<td>369</td>
</tr>
<tr>
<td>Toluene</td>
<td>24</td>
<td>92.15</td>
<td>2219</td>
<td>2214</td>
</tr>
<tr>
<td>Pentane</td>
<td>88</td>
<td>72.15</td>
<td>6384</td>
<td>4151</td>
</tr>
<tr>
<td>TCA</td>
<td>180</td>
<td>133.41</td>
<td>23970</td>
<td>3019</td>
</tr>
<tr>
<td>Propane</td>
<td>180</td>
<td>44.11</td>
<td>7925</td>
<td>--</td>
</tr>
<tr>
<td>Butane</td>
<td>75</td>
<td>58.12</td>
<td>4352</td>
<td>--</td>
</tr>
</tbody>
</table>

The compounds trichloroethane, propane, butane, pentane and toluene may react via a bond breaking mechanism [1]. The molar specific energy ($S_m$) for decomposing these compounds is indeed much higher than for decomposing styrene, ethylene and NO. This supports the idea that the bond breaking mechanism needs more energy.

**Reactor analysis**

To examine the model, which describes the reaction in an ideal plug flow corona reactor, we made a comparison between the calculated conversion (eq.4) and the measured conversion. The model correctly calculates the conversion in the cases of: styrene, toluene, 1,1,1-trichloroethane, NO and pentane. Although ethylene shows scattering around the Y=X line, the calculated conversions are in the same area as the measured conversions. The calculated conversions for butane and propane do not fit the experimental data. The purpose of this model is to make a reactor design based on a limited number of measurements. The fit parameter in the model is the activation energy for the mixture. Table 2 shows the activation energy for those reactions where the model fits the experimental data. If we compare the activation energies with the specific power (S) for 63% conversion in Table 2, we see that TCA changed ranking with pentane, and that NO changed with ethylene.

**Conclusion**

1. Our industrial prototype corona reactor decomposes dilute concentrations of VOCs in an air stream in an energy efficient way.
2. To predict the decomposition of VOCs in the reactor we made a model based on known parameters and on activation energy. The model correctly describes the conversion for most VOCs.
3. The model shows that the conversion is depending on a combination of parameters: specific power (kWh/kg), residence time in the reactor, inlet mass flow VOC, molar gas density, total volume of the reactor, and the activation energy for the mixture air+VOC.

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**References**


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