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BTEX (Benzene, Toluene, Ethylbenzene and Xylene) Degradation by Cold Plasma

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***Abstract*—**The volatile organic compounds - BTEX (Benzene, Toluene, Ethylbenzene, and Xylene) petroleum derivatives, have high rates of toxicity, which may carry consequences for human health, biota and environment. In this directon, this paper proposes a method of treatment of these compounds by using corona discharge plasma technology. The efficiency of the method was tested by analyzing samples of BTEX after going through a plasma reactor by gas chromatography method. The results show that the optimal residence time of the sample in the reactor was 8 minutes.

***Keywords*—**BTEX, Degradation, Cold plasma.

I. Introduction

VOLATILE organic compounds - VOCs can impact in all spheres, both in the physical (due to emissions of VOCs to ozone formation), in the biotic (due to damage to fauna and flora caused by the emission of VOCs) and in the anthropogenic (because people's exposure to hydrocarbons caused by the emission of VOCs).

Among the many studies on the determination of VOCs, there is an increased interest for compounds benzene, toluene, ethylbenzene and xylene, known as BTEX, because their high rates of toxicity [1]. Exposure to these compounds, depending on the concentration and duration of exposure, can cause health ranging from fatigue, irritation of the nose, eyes and throat, weakness, mental confusion, seizures, coma and death to serious risks, with benzene considered the most toxic as potentially carcinogen. However, toluene is found in higher concentrations compared with the other constituents of BTEX [2].

BTEX contamination is related to products derived from petroleum, such as gasoline which has in its composition about 10 to 59% aromatics [3], and these monoaromatic hydrocarbons are the most soluble and the most mobile constituents of the gasoline fraction [3], [4].

Aware of this situation, this paper applies the technology of cold plasma or corona discharge to degrade BTEX. This degradation is possible due to the high-energy resulted by corona discharge, thus providing a good decomposition efficiency.

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The processes using the corona discharge, are also known as "corona plasma" or "cold plasma". This process is called as a partially ionized gas in which the mean energy of the electrons is considerably higher than that of the ions and gas molecules. The energy produced to generate cold plasma is very small being proportional to the increase in temperature that is close to 25ºC.

A corona discharge is created by applying a series of high voltage pulses applied to a thin coaxial wire located inside a metal tube. A typical discharge cold plasma is incandescent or serpentine.

Once generated the ionized gas, the electrons collide with gas molecules, creating chemically active species known as radicals. The radicals, once produced, can react with pollutant molecules in the gas stream, breaking them down into less harmful compounds or compounds easily handled [5].

The process of cold plasma has a very strong chemical reaction that may reduce and decompose toxic contaminants in the gas phase. The ability of plasma oxidation is stronger than ozone and key points for the practical use of the process are process reliability, energy efficiency (economic) and plasma treatment of post-processed gases by plasma [6].

II. Materials and Methods

The methodology consisted of three steps; mounting the reactor, degradation of BTEX, and gas analysis.

A. Assembly Reactor

The body of the reactor consisted of a cylindrical quartz tube, coated aluminum foil, which served as one of electrodes in the center of the quartz tube was fixed a bolt of stainless steel, which served as the other electrode. It is worth highlighting that screw is fixed in two stoppers located at both ends of the quartz tube, which besides serving to seal the exits, keep the electrode (screw) in the center of the tube (Fig. 1).

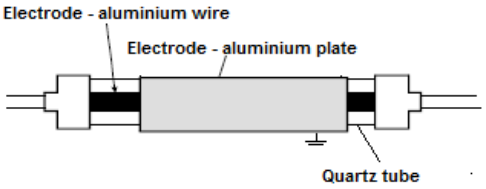

Fig. 1 Plasma reactor with annular cylindrical electrodes

B. BTEX Degradation

To check the efficiency of the reactor, experiments with volatile organic compounds BTEX were performed. The

compound was entrained by compressed air into the reactor after being volatilized within a bottle scrubber (Fig. 2). The volatilization may or may not be controlled via a temperature-controlled electric heater, placed under the bottle washer. The BTEX being inside the reactor is subjected to plasma exposure.

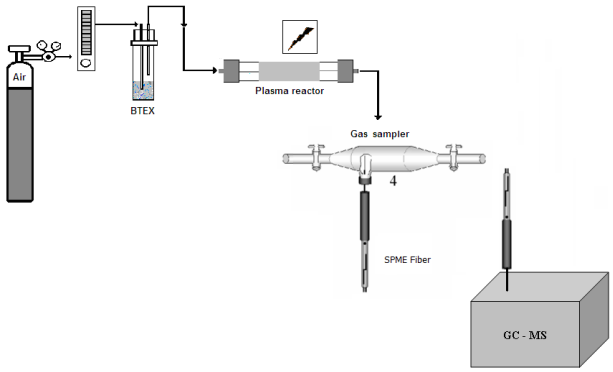

Fig. 2 Cold plasma system for BTEX removal

The sample deposited on the spray bottle BTEX is entrained by a flow of compressed air with a flow rate of 1L.min^{-1} gas to the cylindrical quartz reactor. The compressed air, as well as carrier gas, was also employed as plasmagen gas, due to the formation of ozone, making a strong oxidant.

For the decomposition of BTEX by cold plasma, tests were made with the outputs of the closed ampoules. The introduction of liquid samples in cold plasma reactor was performed by spraying and dragging these with compressed air.

The blank of BTEX was run past BTEX, after evaporation with controlled temperature, in the reactor with the discharge turned off (prior to decomposition).

During the time of contact with the plasma, both input and output of the reactor were kept closed during times of 8, 10 and 12 minutes, so that the products of fragmentation of BTEX were absorbed by the SPME fiber and desorbed in the gas chromatograph injector.

C. Gas Analysis

The gas resulting from the monitoring process was conducted by SPME technique, where the gases are adsorbed on a fiber polydimethylsiloxane (PDMS) of 100mm thick obtained from Supelco (Bellefonte, PA, USA) and desorbed in split-splitless injector of Shimadzu gas chromatograph, model GC-14B, equipped with FID detector. A capillary column 30m x 0.25mm and thickness of 0.25µm was used.

The temperature used for GC analysis was 40°C, hold for 1min using a heating rate of 10°C min^{-1} to 100°C, then held at a heating rate of 15°C min^{-1} to 180°C. The pace of the running total was 120min. The temperatures of the injector and detector were 280°C.

III. Results

Figs. 3-5 show the chromatograms obtained from samples of BTEX for different times, and the sample A refers to the blank and sample B BTEX to the decomposition of BTEX in accordance with specified time. The order of elution is: benzene, toluene, ethylbenzene, and xylene, as the low-molecular weight compounds elute first. The overlay of the chromatograms relative to white BTEX allows better visualization of the reduction peak.

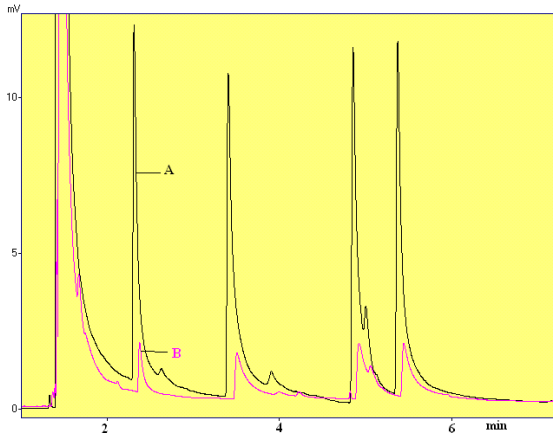

Fig. 3 Chromatogram of BTEX analysis (A- Blank of BTEX, B-BTEX 8min)

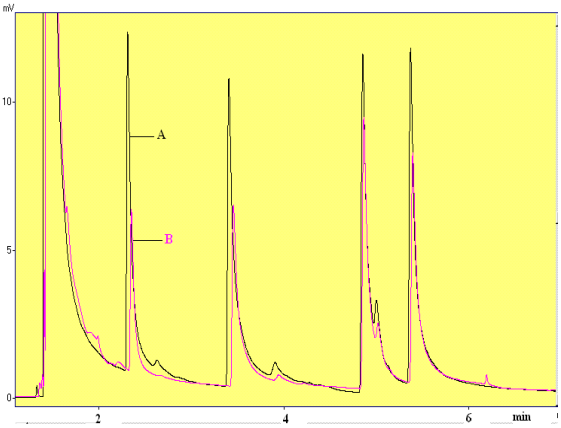

Fig. 4 Chromatogram of BTEX analysis (A- Blank of BTEX, B-BTEX 10min)

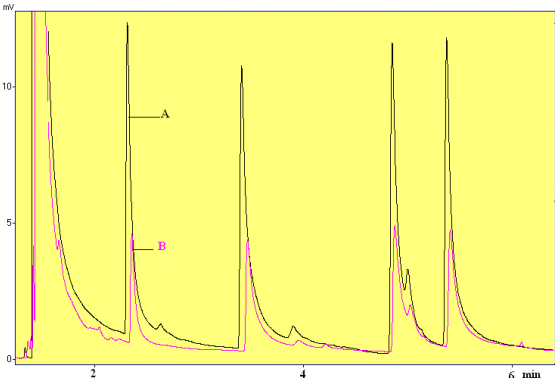

Fig. 5 Chromatogram of BTEX analysis (A- Blank of BTEX, B-BTEX 12min)

As can be seen in Figs. 3-5, reduction in the BTEX with all times analyzed, but the best efficiency in the decomposition of the BTEX compounds were detected in the time of 8min of the contaminant gas in contact with the plasma. According to the results, the best time in contact with the corona discharge is 8min, a longer time is not necessary. Also, as the running time was only 12min, since the beginning, the interest in this study was whether only occur disposal of contaminated gases, it was not possible to analyze the appearance of other peaks corresponding to the products formed by the decomposition. However, since no peak after 12min running was observed, it is concluded that with the fragmentation of BTEX molecules, the product formation is higher chain, appearing in the chromatogram times higher than 12min.

Apparently, there is an inverse relationship between the efficiency of destruction and ionization energy of the compounds. The ionization energy of each of the four BTEX compounds is shown below (Fig. 6).

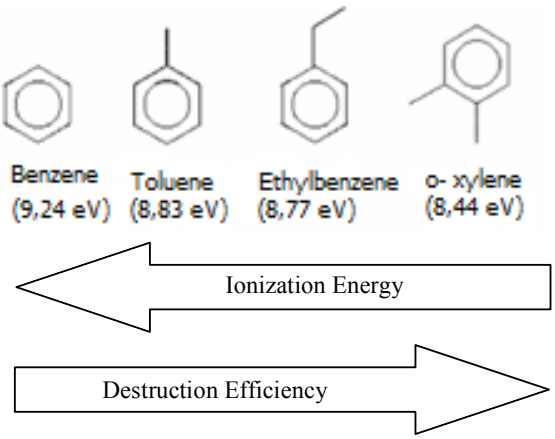

Fig. 6 Relationship between the efficiency of destruction and ionization energy of BTEX compounds

This suggests that the decomposition of the compounds occurs firstly by plasma chemical substitutions on the aromatic ring, where chemical bonds are weaker, so the more substituted compounds destruction efficiency is greater.

Also, for chemically similar compounds (aromatic hydrocarbons), the destruction efficiency is inversely related to the ionization energy and is directly related to the degree of substitution, suggesting that local chemical substitution may have the highest plasma activity.

IV. Conclusion

The cold plasma showed good results in decomposition of the compounds tested, the use of plasma reactors corona discharge for removing gaseous pollutants such as BTEX to be viable. Furthermore, the maintenance of these reactors is minimal, and can be built with inexpensive materials.

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