Research Article

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Studies on the Electrical Behaviour and Removal of Toluene with a Dielectric Barrier Discharge

Abstract: This contribution attempts to establish an easy-to-apply non-thermal plasma reactor for efficient toluene removal. Derived from the already established knowledge of the so called Dielectric Barrier Discharge (DBD) Stack Reactor a new model reactor was used in this work. The DBD Stack Reactor is a multi-elements reactor but in this work only one stack element was used to investigate the efficiency and efficacy of toluene removal. In case of reliable results the scalability process for industrial application is already well known. Therefore, laboratory experiments were conducted in dry and wet synthetic air with an admixture of 50 ppm toluene. Along with the toluene removal process the electrical behaviour of the discharge configuration was investigated. It was found that the electrical capacitance of the dielectric barrier changes with variations of the operating voltage. This could be due to the changes in the area of the dielectric barrier which is covered with plasma. Additionally, it was found that the power input into the plasma, at a fixed operating voltage, is proportional to the frequency, which is in agreement with the literature.

Regarding the decomposition process, the total removal of toluene was achieved at specific input energy densities of 55 J L^{-1} under dry conditions and 110 J L^{-1} under wet conditions. The toluene removal was accompanied by the production of nitric acid (dry conditions) and formic acid (wet conditions). The latter suggested a combination of the plasma reactor with a water scrubber as an approach for total removal of pollutant molecules.

Keywords: non-thermal plasma, dielectric barrier discharge, capacitance, toluene removal

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1 Introduction

Volatile Organic Compounds (VOCs) are a class of contaminants that are mainly present in different industries from semiconductor manufacturing plants to chemical processing plants including paints, coatings, polymers, oil refineries and other chemical manufacturing. The large emission of these compounds in the atmosphere contributes mainly to the production of photochemical smog and to certain health problems like nausea, skin irritation and risk of cancer [1,2]. The removal of dilute VOCs from air is still one of the main tasks of health and environment protection. Conventional methods for VOCs removal include thermal oxidation, condensation, absorption and biofiltration. The thermal oxidation and condensation are economically viable only for moderate to high VOCs concentrations [3]. The absorption process does not destroy VOCs but simply transfers them to another medium, and in addition, this technology suffers from problems arising from deposits of dirt and clogged filters [4]. Bio-filters are useful only for VOCs that have a certain solubility in water and they are cost-effective if the volume of air to be treated is in the range of 10^4–10^5 m^3 h^{-1} [5].

Nowadays, among all the techniques already used for air depollution, the Non-Thermal Plasma Technology (NTPs) is one of the most promising regarding the treatment of high volume and small concentrations of VOCs-containing air with low energy cost impact [6,7]. Many reactor configurations have been developed to generate an NTP at atmospheric pressure, such as corona discharge, dielectric barrier discharge and packed bed discharge to decompose many different VOCs as summarized by Kim and Vandenbroucke et.al. [8,9]. This study is devoted specifically to the destruction of toluene which is one of the most prevalent hydrocarbons in the troposphere because of its massive production and of the broad and widespread use in the world. Toluene is widely used in many industrial applications, not only as a feedstock for chemical processes (medicine, dyes, and explosives) but also as a solvent (thinner, paints, lacquers, adhesives, and detergents). Exposure to toluene in air is

known to affect the central nervous system and may cause tiredness, confusion, weakness, memory loss, nausea, and color vision. These symptoms usually disappear when exposure is stopped, although inhaling high levels of toluene in a short time may cause light-headedness, nausea or sleepiness. Dielectric Barrier Discharges (DBDs) are commonly used to produce NTPs at atmospheric pressure, and this technology is used in industry for ozone generation [10]. The mean energy of the free electrons ranges from 1 to 10 eV, whereas the actual gas temperature remains near ambient temperature which is cool enough to provide a noncorrosive processing environment while still supporting a multitude of chemical reactions leading to the decomposition of the pollutants. Through electron-impact ionization, dissociation, and excitation of the source gases, active radicals and ionic and excited atomic and molecular species are generated, which can initiate plasma chemical reactions [11]. A great advantage of DBDs over other discharges is that the average energy of the electrons can be optimized by changing either the geometry of the electrodes or the type and thickness of the dielectric material, which means the reaction conditions of plasma processing can be optimized in order to facilitate the scalability for industrial application purposes.

The abatement of toluene with NTP is already widely studied as well as with or without the combination of various catalysts [12,13]. In this paper, the authors report the first experimental results obtained for toluene destruction in a novel dielectric barrier discharge reactor. The base technology was developed at the Leibniz Institute of Science and Technology (INP Greifswald/ Germany) by Müller et. al [14]. Instead of using either the so-called Surface Discharge Dielectric Barrier Discharge reactor (SD-DBD) or Stack Reactor, the authors used only a single element consisting of two metal meshes and a dielectric plate in between the two electrodes. The present study reveals that the new reactor is an energy-efficient technology for complete VOC remediation in air and at the same time, the formation of byproducts such as NO_x is strongly suppressed. The experiments performed at different power and humidity settings give information about the main chemical mechanism by which toluene is decomposed within this reactor.

2 Experimental Procedure

The experimental setup used is depicted in the left part of Fig. 1. The gas mixture to be treated was produced with gas cylinders (Air Liquide, N_2, O_2, and 517 ppm_v C_7H_8 balanced with N_2). The total gas flow was 75 L h^{-1} (60 L h^{-1} N_2 and N_2-C_7H_8 mixture + 15 L h^{-1} O_2). For the experiments under dry conditions the oxygen was added directly to the gas mixture. For the experiments under wet conditions the oxygen was directed through a water containing bubbler. Thus, a water content of around 0.5% was generated. The gas mixture was directed to the plasma reactor consisting of two stainless steel-made wire mesh electrodes separated by a plate made of phlogopite (a type of mica) acting as the dielectric barrier. This so-called stack configuration [14] with the size of 110 x 80 x 3 mm was placed in a plexiglass housing containing the gas inlet and outlet connectors as well as the electrical connections (Fig. 1, right). The inner dimensions of this housing were 200 x 120 x 12 mm. This resulted in a semi-indirect plasma treatment of the gas mixture because most of the gas flowed along the electrodes configuration instead of entering the active plasma region between the electrodes and the dielectric barrier as depicted by the arrows in Fig. 1. An advantage of this configuration is the very small back pressure, which is desired for the treatment of large gas flows in industry.

The plasma reactor was energized with a programmable high-voltage power source (Chroma 61604) and a high-voltage transformer. The power dissipated into the plasma was analyzed by recording the high voltage operating the reactor with a digital oscilloscope (Tektronix DPO 4104) via a high voltage probe (Tektronix P6015A). Additionally, the voltage drop over a capacitor (capacitance 100 nF), connected in series with the reactor between the grounded electrode and protected earth, was recorded. By multiplying the voltage drop over the capacitor with the capacitance the transferred charge was obtained. Plotting the transferred charge against the applied voltage delivered a so-called charge-voltage plot (also known as Lissajous-figure), which will be discussed in more detail in the next section.

Samples of the gas mixture were analyzed by FID (Flame Ionization Detector, Testa 2010T), measuring the amount of carbon atoms bond in hydrocarbon molecules. Additionally, an FTIR spectrometer (Fourier Transform InfraRed spectrometer, Bruker Alpha, spectral resolution 1 cm^{-1}, optical path length 5 m) was used to monitor the processed gas mixtures. The gas cell of the spectrometer was heated up to 40°C in order to avoid water condensation. In addition, since a large amount of ozone was produced, increasing the temperature of the spectrometer cell could lead to further unwanted reaction because of the thermal instability of the ozone.
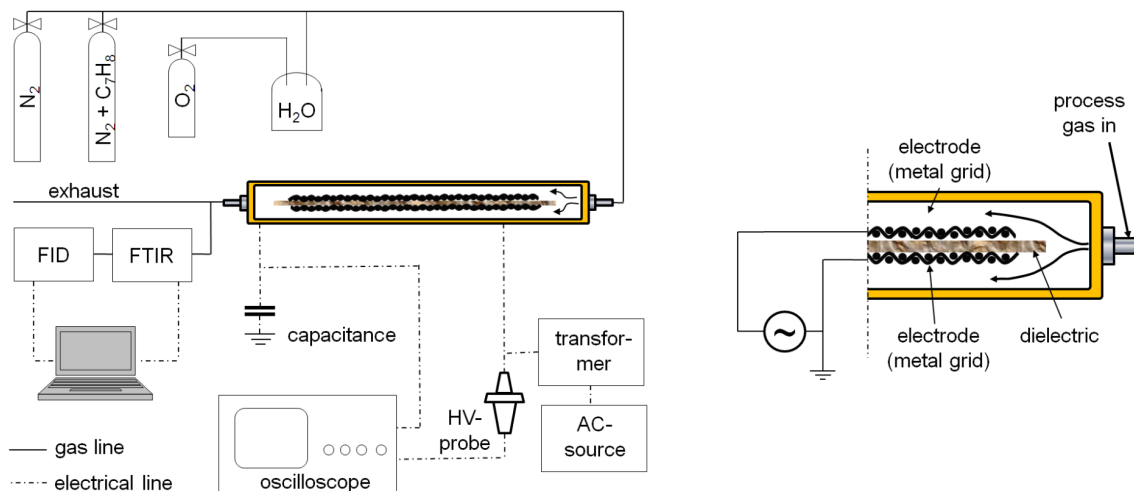
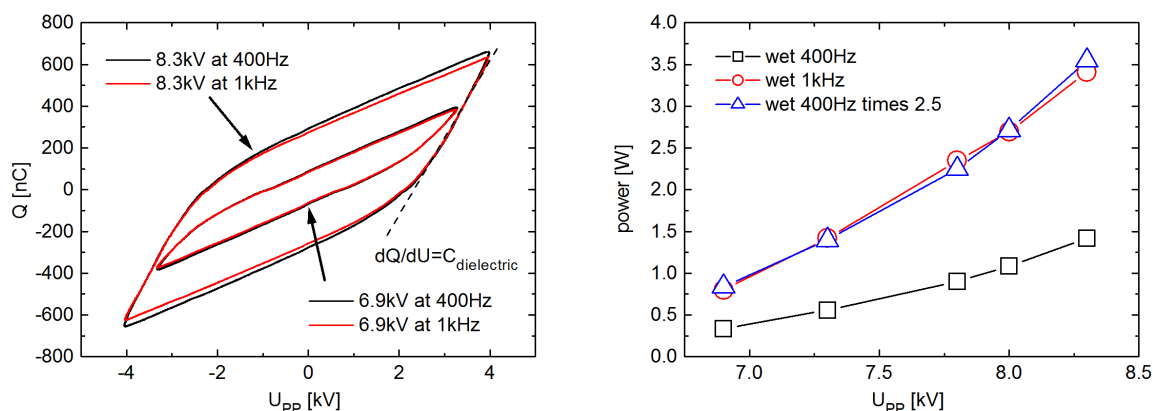**Figure 1:** Experimental Setup (left) and detailed horizontal cut view of reactor (right).

Figure 2: Left: Q-V plots recorded at 8.3 kV and 6.9 kV at 400 Hz and 1 kHz under wet conditions; Right: Power input under wet conditions at 400 Hz and 1 kHz and at 1 kHz calculated based on the power input at 400 Hz.

3 Results and Discussion

3.1 Electrical behaviour of the electrode configuration

In order to obtain comparable results of the measurements under the selected conditions the authors have chosen the operating voltage as the electrical parameter to be set for every measurement. The electrical data recorded during the experiments were investigated during the analysis procedure. The power input into the plasma reactor was calculated by integrating the area of the charge-voltage plot (Q-V plot) and multiplying the resulting value with the frequency of the applied voltage [10,14]. By doing this, it was found that the Q-V plots for different frequencies at the same driving voltage were

almost identical. Examples are given in the left part of Fig. 2. The black curves show the Q-V plots recorded at a frequency of 400 Hz, whereas the red curves display these recorded at 1 kHz. The operating voltage was 8.3 kV and 6.9 kV, respectively. The equality of the Q-V plots implies that the energy transferred per cycle into the plasma was identical. Thus, the power input for a fixed operating voltage should depend only on the frequency in a linear manner [10,14]. Using the frequency ratio of 2.5 (1000 Hz divided by 400 Hz) and multiplying it with the power input measured at 400 Hz, one obtains the calculated power at 1 kHz. In the right part of Fig. 2 the power measured at 400 Hz (black boxes), the power calculated for 1 kHz (blue triangles) and the power measured at 1 kHz (red circles) are shown. The values calculated and measured at 1 kHz are in good agreement and can
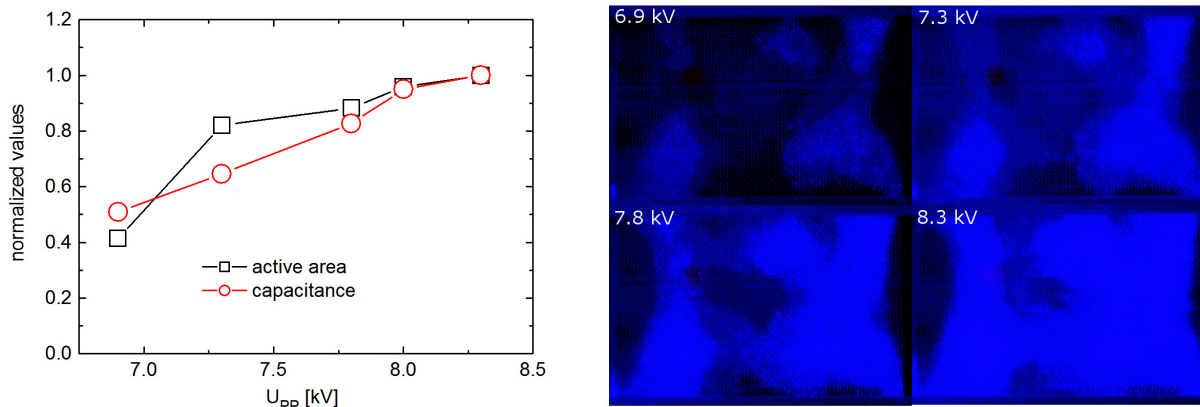
Figure 3: Left: Increase in active plasma area and increase in capacitance with respect to the operating voltage; Right: Photographs of the plasma operated at different voltages.

be taken as another evidence of the proportionality of frequency and power already mentioned by Kogelschatz and Manley [10,15].

Further investigations showed that the slope of the charge-voltage plot, from the bottom right corner to the upper right one, which gives the capacitance of the plasma reactor during the discharge period, increases with increasing the operating voltage (Fig. 2, left). The authors suggest that the reason is the increase in the active area of the electrode, which means the surface of the electrode covered with plasma. Photographs of the plasma were taken (Nikon D5100, aperture 5.6, exposure time 30 s) and reworked with an image manipulation program (Gimp 2.8, color correction) to make the plasma visible (Fig. 3, right). An analysis of the extension of the visible plasma was performed. The obtained values were normalized as well as the values of the measured capacitance. The result is given in the left part of Fig. 3. The normalized capacitance (red circles) increases linearly with the increasing driving voltage. Except for the value at 7.3 kV, the normalized active area of the plasma (black boxes) also increases almost linearly so it can be taken as a good affirmation for the given hypothesis. This is further confirmed by the fact that the bottom right corner, as well as the left top corner of the Q-V-plot (which both correspond to the inset of the discharge in every half period of the applied voltage), are not sharp. This would be the case for a uniform breakdown of the gas discharge.

3.2 Toluene Removal

An FID was used as the main analytical instrument to analyze the toluene content in the gas mixture to be treated. Although an FID does not distinguish between different hydrocarbons, its use is justified because an FID is not sensitive to the main components produced by toluene removal (carbon monoxide, carbon dioxide, formaldehyde, and formic acid [16]). With the concentration of toluene at about 50 ppm_v in the untreated gas mixture, the molar fraction was calculated and plotted against the SED (Specific Energy Density), which was calculated by dividing the power input into the plasma with the gas flow. The SED is often used as a parameter for the comparison of the efficiency of different plasma sources used for gas processing or exhaust treatment. The results are shown in Fig. 4. The removal efficiency increases with SED up to the total removal at around 55 J L^{-1} under dry conditions (black boxes) for both frequencies. Under wet conditions (red circles) the removal efficiency is less. The SED needed to achieve complete removal of toluene under wet conditions is almost twice the one needed under dry conditions. The complete removal under wet conditions is only achieved at 1 kHz (right graph). At 400 Hz (left graph) the required SED value was not achieved even at the highest operational voltage used. On the one hand, the removal efficiency strongly depends on the humidity conditions (dry or wet). On the other hand, under wet conditions, there is also a dependency on the frequency found, which did not appear under dry conditions.

The values in Table 1 are found by calculating the energy density parameter β via equation (1):

$$[C_7H_8] = [C_7H_8]_0 \cdot e^{\left(-\frac{SED}{\beta}\right)} \tag{1}$$

The energy density parameters obtained under dry conditions are very similar, whereas those obtained under wet conditions differ significantly.
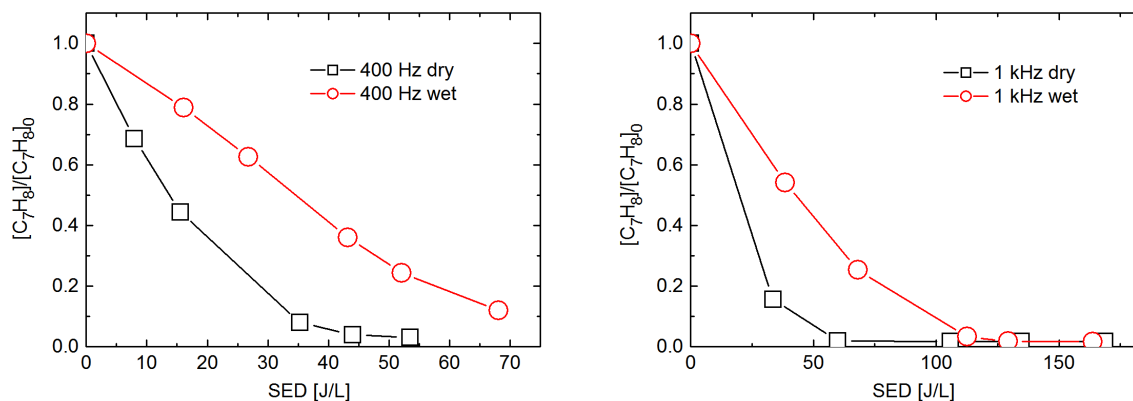
Figure 4: Molar fraction of toluene under dry (black boxes) and wet (red circles) conditions at 400 Hz (left) and 1 kHz (right).

Table 1: Energy density parameters for the different settings investigated.

frequency	condition	β [J L^{-1}]
400 Hz	dry	17.09
1 kHz	dry	17.77
400 Hz	wet	33.02
1 kHz	wet	48.59

In order to get a better insight in the toluene removal process the infrared absorption-spectra were recorded. In Fig. 5 samples of selected spectra are presented showing the so-called fingerprint region (wavenumber = 1500–700 cm^{-1}). The left graph shows the infrared-spectra taken at the applied voltage amplitude of 8.3 kV$_{PP}$ and the frequency of 1 kHz under dry conditions. In the untreated gas mixture (black curve) the absorption band related to toluene is the only detectable band of importance. With plasma (red curve), the strong absorption band of ozone, which is the main stable product of an NTP operated under ambient conditions, appears at 1053 cm^{-1}. Additionally, nitric acid is detected, which is assumed to be the product of the reaction of the intermediate NO$_x$ with hydroxyl radicals produced by the toluene decomposition. The toluene absorption band is replaced by a broad absorption band whose origin could not be identified. Because no infrared absorption spectrum of the known products or intermediates (formaldehyde, benzaldehyde, benzoic acid, benzene, nitrobenzene, phenol, formic acid, and acetic acid [13]) of the toluene removal process fits the recorded spectra, it is assumed that it is a compound emitted either from the material of the reactor housing (plexiglass) or the dielectric barrier

(phlogopite). According to the results given by the FID this analyzed gas mixture does not contain any hydrocarbons at all.

Under wet conditions (right graph, same electrical parameters) there is no detectable nitric acid. Moreover, the absorption of ozone decreases significantly. Both is assumed to be due to the consumption of energetic electrons, which under dry conditions are used to produce NO$_x$, as a necessary intermediate for the production of nitric acid, by water dissociation and vibrational excitation. These changes result in a remarkable production of formic acid which is soluble in water. The lower efficiency in toluene removal under wet conditions is also assumed to be due to this. Because of the construction of the NTP-reactor, with the electrode configuration in the middle of the discharge reactor and, therefore, a huge gas volume not in direct contact with plasma, the toluene to be removed hardly comes in contact with plasma. Thus, electron dissociation cannot be the main process. The oxidation by ozone is of minor importance as well because of the small rate coefficient of this reaction (k = 1.2·10^{-20} cm^3 molecule^{-1} s^{-1} [17]). Therefore, the reaction with atomic oxygen (k = 7.6·10^{-14} cm^3 molecule^{-1} s^{-1}) is thought to be the most important removal process [17]. Since for the production of these species the energetic electrons are needed, the lower efficiency under wet conditions can be explained by their lower production efficiency due to the consumption of these electrons, as well as a reduction of the electron temperature by water dissociation and vibrational excitation.

More detailed discussion of toluene removal, including carbon balance and selectivity discussion, are needed to clarify these questions, which remains for future investigations.
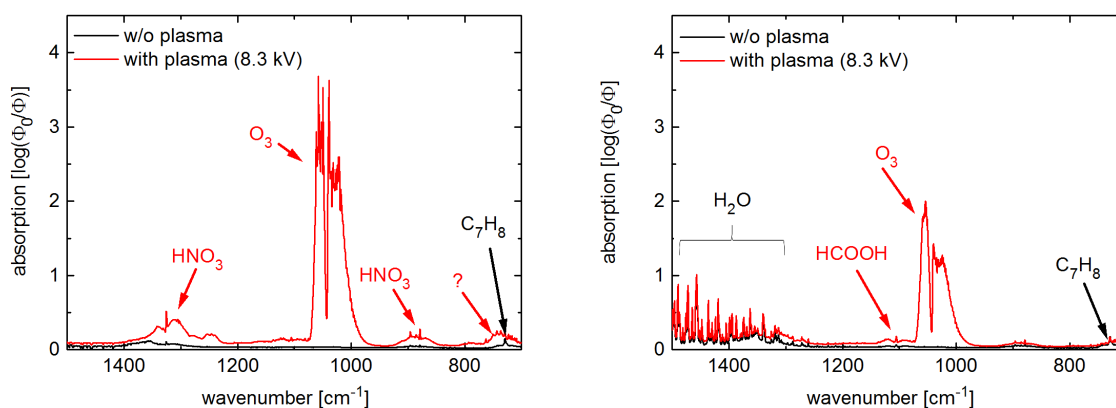
Figure 5: Samples of the infrared-spectra of the analyzed gas mixtures without plasma (black lines) and with plasma (frequency 1 kHz, operating voltage 8.3 kV, red lines) under dry (left) and wet conditions (right).

4 Conclusions

In this contribution an easy-to-use and easy-to-set-up NTP-reactor, based on the conept of the DBD stack reactor, was investigated for toluene removal. Along with the analysis of the toluene removal process, the electrical behaviour of the electrode configuration and the appearance of the plasma itself were investigated. It was found that the electrical capacitance of the dielectric barrier increases with increasing the operating voltage amplitude. This could be explained by an increase in the active plasma area, which is the area of the dielectric barrier covered with plasma, and therefore, by an increase in the active area of the dielectric barrier discharge.

By means of FID-measurements it could be shown that the total removal of toluene was achieved at specific energy densities of around 55 J L^{-1} (corresponding to 13.5 g kWh^{-1} of energy yield) under dry conditions and of around 110 J L^{-1} (6.7 g kWh^{-1}) under wet conditions. Suprisingly, the energetic efficacy is dependent on the applied frequency in case of wet conditions. The FTIR analysis revealed the formation of formic acid as a product of the toluene removal process under wet conditions, which was not found under dry conditions. In that case a remarkable production of nitric acid was found which, vice versa, did not take place under wet conditions.

Making a comparison with some of the references presented in [9] (Table 4) about the toluene decomposition with NTP alone, the desired energy density is comparably low with this set-up even at low initial concentrations and at humid conditions. In addition, the energy yield obtained with this reactor under dry condition is the highest and under humid condition the value is still one of

the highest, whenever to accomplish the same yield value with a different set-up the energy density obtained is one order of magnitude bigger.

The total removal of toluene under wet conditions, along with the production of formic acid, which is soluble in water, suggests that the combination of the DBD-reactor, investigated in this study, with a water scrubber could be a powerful, efficient, and easy to apply tool for toluene removal.

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