Analysis of contamination level of gases generated during the surface cleaning process of metal sheets with low-pressure cold plasma

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Abstract. The research addresses an analysis of the level of contamination generated by the gases produced when applying low-pressure cold plasma in a cleaning process of metal sheets used in the manufacture of white goods. A mixture of argon and oxygen ionized gases at 50% was utilized to break down the lubricating oil molecules deposited on the surface of the sheet metal. A statistically significant number of samples were selected, with different volumes of oil on the surface, between 6 ml and 34 ml. The samples were later subjected to a plasma discharge with a time of 72 s, a gas pressure of 0.6 bar and 50% power to determine the correlation of the oil volume with the levels of gases generated by the discharge, maintaining the degree of surface cleanliness, as given by contact angle values between 67.5 and 79 degrees, constant. For the analysis of results a Pearson correlation was applied for each detected gas. An analysis was later conducted of the relationship between the degree of cleanliness of the metallic surface, as given by contact angles at 16, 36 and 53 degrees, with the levels of the gases generated by the plasma discharge, keeping the volume of the lubricating oil on the surface constant at 5 ml. For the analyses, statistical tests were carried out to find the correlation between the predictor variables and the dependent variable to establish a multivariate linear statistical model. The results allowed the behavior of the level of contamination to be determined, establishing that the volume of oil does not influence the level of the gases generated by the use of low-pressure cold plasma. The results obtained allow us to understand the relationship between the contact angle that represents the quality of surface cleaning of oil-impregnated sheet metal and the level of contamination generated in the process.

1 Introduction

In the surface cleaning process of metal sheets, the use of acids and bases are considered toxic and dangerous because of their high corrosivity which can harm health, infrastructure, and the environment. Etching baths produce acid emissions and nitrous gases, the latter of which are considered highly toxic [1–3]. The use of this process with this traditional technology has not been able to be replaced due to its efficiency in the degree of surface cleaning and low production costs. The efficiency of the degreasing and etching process in the cleaning of metal sheets is determined by the surface free energy which directly depends on the contact angle formed by a
test liquid and the analyzed surface where the varying conditions of each process must be taken into consideration [4–12]. Previous studies have shown that the application of low-pressure cold plasma in the surface cleaning of metal sheets presents satisfactory results in the removal of oil [5–7]. Easy to handle, non-polluting gases are used for plasma generation [8], to remove all unwanted residues such as oxides and organic contaminants. Therefore, the adhesive property of the material, represented by the contact angle that is directly related to the surface free energy, will depend on the efficacy of this treatment [6, 9, 10]. Currently, technological advancement in the generation of low-pressure cold plasma has allowed the surface free energy indices in sheet metal cleaning to be reached and improved [11, 13]. In this context, the investigation aims on determining the level of gas byproducts generated during the plasma cleaning of sheet metal which can be an alternative to the traditional process of cleaning through acid bath immersion.

2 Experimental work

2.1 Equipment used

2.1.1 Plasma generator. For the investigation, a Diener Electronic PICO Low Pressure System series plasma generator was used. It contains a 50 cm wide, 70 cm high and 50 cm long, electrical cabinet. The working chamber has a diameter of 150 mm, a length of 320 mm, a volume of approximately 5 liters and 3 needle-operated gas feed channels. The 13.56 MHz/0-100 W electric generator has a Leybold Trivac E2 vacuum pump with a flow of 2.5 m$^3$/h and 2 x 10$^{-3}$ mbar of pressure. The control system is semi-automatic, with the duration of the process is controlled by timer. There is a sample carrier within the plasma generating (working) chamber. The chamber is subsequently sealed to create a vacuum prior to the entry of the gas that will be ionized with the ideal parameters for generation, the same that have been determined in previous research by Sarmiento [5].

2.1.2 Gas analyzer. The gases generated in the cleaning of the sheet metal were detected by a QROTEC QGA 6000 analyzer that is configured with the dispersive infra-red (NDIR) method to analyze carbon monoxide (CO), hydrocarbons (HC), and carbon dioxide (CO$_2$) in percentages and an electrochemical method to analyze diatomic oxygen (O$_2$) and nitrous oxides (NOX) in parts per million. In the NDIR analysis method, a source of infrared rays is located at one end of the sample bank and at the other end, a sensor is attached to detect the component of a gas and calculate its density.

2.1.3 Digital goniometer. A CAM 100 digital goniometer was used to measure the contact angle. The goniometer takes 60 images per second and includes software for measuring the contact angle and calculating the surface free energy. It can determine angles between 0 and 180 sexagesimal degrees, formed by the drop of the liquid and the surface of the sheet.

2.1.4 Lubricating oil. The mineral oil used in mechanical forming is LUBE HD-2 which is obtained by refining petroleum and stands out for its stable viscosity, lubricating capacity, fluidity and ability to dissipate heat among others. Table 1 presents the main technical characteristics thereof.
2.2 Methodology

2.2.1 Procedure. To determine the polluting gases generated in the cleaning of the oil impregnated sheet metal through the application of low-pressure cold oxygen and argon plasma, 162 representative samples were used according to the study population. They were randomly selected to determine the behavior of the level of gas emissions generated with respect to the amount of oil on the surface of the sheet metal. The samples have a dimension of 5 cm per side with a thickness of 1 mm so that they can fit in the generating chamber. The chamber is programmed with the parameters presented in Table 2 that generate a contact angle between 67.5 and 79 degrees to analyze the contamination according to the volume of polluting oil on the surface, which varies between 6 ml and 34 ml. The generator is connected to the gas analyzer that determines the different emission levels.

To establish the influence of the contact angle at 16, 36 and 53 degrees in the contamination level of the gases generated in the cleaning, the same sample size was used, 162 metallic sheets, each impregnated with 0.5 ml of oil with the plasma generation parameters presented in Table 2. To determine the impact of the volume of oil and the contact angle in the level of contamination, 27 samples were used in three groups according to the polluting gas with 3 different volumes of oil and contact angles.

| Table 2. Parameters of the plasma generator. |
|---------------------------------------------|
| Parameters | Contact angles |
|-------------|----------------|
|             | 67.5-79°       | 16° | 36° | 53° |
| Pressure    | 0.6 bar        | 0.6 bar | 0.6 bar | 0.6 bar |
| Time        | 72 s           | 600 s | 360 s | 240 s |
| Power       | 50%            | 90% | 70% | 60% |
| Gas (Ar/O)  | 50/50          | 50/50 | 50/50 | 50/50 |

2.2.2 Statistical analysis. To verify the hypothetical assumptions posited in the investigation and to systematize the relationships expected to be found on the correlation between the volume of oil and gases generated, the statistical hypotheses $H_0 = 0$ and $H_1 \neq 0$ were made. To verify (or disprove) the statistical hypotheses, the use of the Pearson correlation coefficient was proposed, as it allows a relationship to be established between the two quantitative variables; a variation in the value of one causes a the value of the covariate to change (value that indicates the degree of joint variation of two random variables with respect to their means). In the hypotheses put forward where the goal is to find a relationship between the contact angle and the level of gases generated the Friedman test was employed for more than two dependent samples where the hypotheses establish if there is a difference or not between the groups. To evaluate the
effect of the oil volume and the contact angle on the contamination level of different gases and predict their value, a multiple linear regression model was proposed, considering that there is no autocorrelation when evaluating the Durbin Watson coefficient and likewise there is no multicollinearity when evaluating the variance inflation factor (VIF).

3 Results and discussion

When cleaning the sheet metal, CO2, CO and HC gases were detected by the gas analyzer. A statistically significant correlation of 96.3% was established between oil volume and carbon monoxide while the correlation between oil volume and carbon dioxide was found to be 88.2%, as can be observed in Figure 1 and Figure 2.

The correlation between oil volume and hydrocarbons was determined to be 70.7%. Figure 3 shows a tendency of increasing hydrocarbons, in parts per million, as the volume of lubricating oil removed from the surface of the sheet metal increases.

![Figure 1](image1.png)  
**Figure 1.** Variable correlation: Oil volume – %CO.

![Figure 2](image2.png)  
**Figure 2.** Variable correlation: Oil volume – %CO₂.

![Figure 3](image3.png)  
**Figure 3.** Variable Correlation: Oil Volume – HC.
For the analysis of the influence the contact angle has on pollution levels, the dispersion data obtained from the 162 samples for each angle was analyzed using standard deviation. According to the Friedman test value for carbon monoxide levels, it is determined that the value of $\chi^2_F > \chi^2_{crit}$, $(313.944 > 5.99)$, indicating a difference in the levels of carbon monoxide at the different contact angles analyzed, as seen in Figure 4. For carbon dioxide the Friedman value establishes that $\chi^2_F > \chi^2_{crit}$, $(324 > 5.99)$ which indicates that there is a difference in carbon dioxide levels respective to the contact angle at $16^\circ$ but levels are equal at angles of $36^\circ$ and $53^\circ$. In hydrocarbons a value of $\chi^2_F > \chi^2_{crit}$, $(324 > 5.99)$ rejects the null statistical hypothesis and it is accepted that there is a difference in the levels hydrocarbons respective to the contact angles analyzed.

![Figure 4. Contamination level - contact angle box plots. (a) CO box plot; (b) CO2 box plot; (c) HC box plot](image)

For carbon monoxide there is a high multiple correlation ($R = 0.915$) of the variables that make up the linear model, where 83.7% of the CO level variations can be explained by the changes in oil volume and the contact angle. The remaining 16.3% (alignment coefficient) of the CO level behavior would correspond to other factors not included in the multivariate model. The Durbin Watson value is equal to 1.592, which is between the values of 0.629 and 1.699, indicating the independence of errors between the variables (there is no autocorrelation) and that the model is perfectly posited. In the coefficient analysis, the variance inflation factor VIF is 1 for the oil volume and the contact angle, which indicates that there is no multicollinearity, that is,
there is no correlation between the independent variables. A partial and semi-partial zero-order
 correlation analysis showed the oil volume to have a low association with the contamination level,
while on the other hand showing a strong relationship between contact angle and contamination
level. The multivariate model for carbon monoxide is determined by the following Equation 1.

\[ Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + e \]
\[ Y = \beta_0 + \beta_1 \text{(contact angle)} + \beta_2 \text{(oil volume)} + \text{random estimation error} \]
\[ \%CO = 0.660 - 0.007 \text{(contact angle)} - 0.016 \text{(oil volume)} + 0.05586 \]

An R value of 0.888, inferred a multiple correlation of 88.8% between the percentage of
CO2 and its predictors, contact angle and oil volume. Additionally, the R squared value of
0.789 indicates that 78.9% of the CO2 level variations are due to changes in oil volume and
contact angle. It is also determined with the adjusted R squared value that 71.9% of the
CO2 variations are due to independent variables with an estimation error of 0.02650. The
Durbin Watson coefficient of 0.999 indicates that there is independence of errors between the
variables and the model is correctly presented. The FIV value equal to 1, demonstrates that
there is no correlation between the independent variables. A partial and semi-partial zero-order
 correlation shows no correlation, association and relation of oil volume with CO2 contamination
levels, while contrarily the contact angle presents 88.8% correlation to the percentage of CO2
generated through plasma cleaning. The multivariate model for carbon dioxide is determined
by the Equation (2):

\[ \%CO_2 = 0.230 - 0.003 \text{(contact angle)} - 0.000 \text{(oil volume)} + 0.02650 \]

In hydrocarbons, the R value is 0.918 establishing a multiple correlation of 91.8% between
the percentage of HC and its predictors, contact angle and oil volume. The R squared value of
0.842 indicates that 84.2% of the HC level variations are due to changes in oil volume and
contact angle. The adjusted R squared value shows that 78.9% of the variations of the
HC are due to independent variables with an estimation error of 257.587, the Durbin Watson coefficient of 1.018 indicates that there is independence of errors between the variables (there is
no autocorrelation) and the model is correctly presented. The FIV value equal to 1, indicates
that there is no correlation between the independent variables. The partial and semi-partial zero-order correlation shows a 0.4% relation of the oil volume and 91.8% relation of the contact angle
in the level of hydrocarbon pollution. The multivariate model for hydrocarbons is determined
by the Equation (3):

\[ \text{HC (ppm)} = 2560.822 - 32.097 \text{(contact angle)} - 5.820 \text{(oil volume)} + 257.587 \]

4 Conclusions

The results from the experimentation process led to there is a very high correlation of 0.96
between oil volume and carbon monoxide, and a high one between oil volume and hydrocarbons
and carbon dioxide at 0.70 and 0.88 respectively. By decreasing the contact angle from 53° to
16°, carbon monoxide emissions increase by 80%, carbon dioxide by 100% and hydrocarbons by
119%. The multivariate analysis showed the volume of oil to have a 12% affect in the level of
carbon monoxide, less than 1% in hydrocarbons and no influence in the level of carbon dioxide.
The contact angle directly affects the level of carbon dioxide at a magnitude of 88.8% and the
level of hydrocarbons and carbon monoxide are 90% affected.
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