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Relationships Between Indoor Air Pollution and Psychrometric and Effective Factors in the Polyurethane Factories with Emphasis on Methylene Diphenyl Diisocyanate

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Abstract: The object of this study is determination of the relationship between airborne methylene diphenyl diisocyanate (MDI) and selective psychrometric variables. The production of MDI factories were polyurethane adhesives, paints and varnishes and the workers were exposed to MDI in the indoor air. The air samples were collected by midget impinger and multiple regressions model was used to determine the relationship between variables. All of the samplers (midget impinger) were connected to mini personal sampler pump fixed to workstations near the source of pollution based on NIOSH method 5522. The first step in the analysis of a solution is derivatization of isocyanates for the separation through HPLC, for their qualitative as well as quantitative analysis. Air sampling and analysis was performed according to (NIOSH) method 5522 for diisocyanate in air. The results revealed that a correlation between MDI concentration and relative humidity, dry bulb temperature, altitude and dimension of polyurethane factories. Dimension of factories yields reasonable negative relationship, the MDI concentration was ranged from 93.8 to 99($\mu g/m^3$) and statistically significant at 0.0001 level and the relative humidity was ranged from 42.6 to 45% and dry bulb temperature ranged from 28 to 29°C were statistically significant at 0.035 and 0.0001 level, respectively. A statistical predictive model was obtained from multiple regression modeling for MDI and psychrometric parameters. The result of the current study may be useful for the prediction of diisocyanate pollution for polyurethane factories in the same psychrometric condition. This indicates that the MDI concentration is attributed to psychrometric parameters.

Key words: Psychrometric Parameters · MDI concentration · Regression · Diisocyanate

INTRODUCTION

Use of polymers of diisocyanates, with much lower vapor pressure, has been raised. Despite variable physical and chemical properties, including vapor pressure, solubility and particle size, all of the major monomeric, prepolymeric and polydiisocyanate species are capable of inducing asthma in the exposed workers [1, 2].

The high reactivity of diisocyanates leads to very durable bond, but also gives health risks for persons who are exposed to these substances [3, 4]. Crespo and Galan [5] have stated that indoor application of PU products to large areas may result in an exposure near the threshold limit values (TLV).

One of the most frequent used isocyanates is methylene diphenyl diisocyanate (MDI). The main component of commercially used MDI is 4, 4'-methylene diphenyl diisocyanate but several other isomers are also present. Owing to the low threshold limit value (TLV), the normal exposure to isocyanates is low. However, in infrequent incidents in industry, high exposure is expected [6].

The physical properties of polyurethanes depend both upon the structural units used for their construction, namely the diols, triols. During synthesis of isocyanates the structural units are combined together for their preparation [7]. The preparation of polyurethanes is an exothermic process having reaction enthalpies typically in the range of 80 - 90 kJ mol^{-1} [7, 8].

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A diisocyanates study has been conducted by Woskie *et al.* [9] in the auto body repair shops for affecting relative humidity and dry bulb temperature as indoor psychrometric parameters in the polyurethane factories. The two parameters such as altitude and dimension of factory that they were reported that these factors affected on indoor air pollution in the auto body repair shops. But in this study, no work has been done to evaluate the relationship between psychrometric parameters, altitude, dimensions of factory and MDI pollution in the polyurethane factories [10].

The specific goal of this study is to answer the following question: How does the MDI concentration changes with respect to psychrometric and factory factors?

The correlation and regression analysis techniques are useful in investigating these relationships. The relationship between meteorological parameters and pollutant concentrations has been well studied in different parts of the world for different time periods. The effect of relative humidity on the curing and dielectric properties was assessed in the USA polyurethane factories [11].

MATERIALS AND METHODS

Throughout polyurethane factories in this study, 5 MDI factories were selected which have 220 all of them performed foaming or polyurethane foams. There were 200 unexposed workers with population who worked in the office area. The sampling and analysis of isocyanates was based on the method of US National Institute of Occupational Safety and Health [12]. All of the samplers with midget impinger connected to mini personal sampler pump fixed to workstations near the source of pollution. The air sample was collected for 2 h at flow rate of 2 lit/min, in impinger containing a solution of reagent in DMSO in addition with Tryptamine. Reversed-phase HPLC has been the dominant separation technique in isocyanate analysis (NIOSH method no: 5522). The first step in the analysis of a solution is derivatization of isocyanates for the separation through HPLC, for their qualitative as well as quantitative analysis. Air sampling was performed according to (NIOSH) method 5522 for isocyanate in air [13]. Air samples were collected at 2 l/min using a midget impinger sampler (SKC, Eighty Four, PA) and personal sampling pumps calibrated before and after sampling with a Dry Cal DC-Lite primary flow meter (Bios International Co. Pompton Plains, NJ). A KNAUER HPLC was used for air analysis, the HPLC equipment consisted of a high-pressure pump, a variable-wavelength UV detector (VUV-24, Variable single wavelength output) and a loop injector, HPLC columns were made of stainless steel (200 mm long x 5 mm in inside diameter) packed with 5m Nucleosil C18. The air concentrations of MDI were monitored continuously by the midget impinger instrument using a Dimethyl Sulfoxide with Tryptamine reagent and the sampling time for HPLC analyses.

The relation between MDI concentration and psychrometrical variables such as relative humidity and dry bulb temperature also other factors such as dimension of workplaces and altitude can be understood better by using multiple regression models. Possible relationships between these variables were examined statistically using the multiple linear regression method which is appropriate to relate MDI concentration to variables, has the formulation given as follows [14]:

$$SI= B_0 + B_1 D+ B_2 Rh + B_3 Td + B_4 Alt + ei \qquad (1)$$

Where *i* is numbers such as 1,2,3…, n; SI is dependent variable (MDI concentration); B_0 is the intercept; B_1 to B_4 are the model parameters; D is dimension of factory (m^3); Rh is the relative humidity (%); Td is the dry bulb temperature (°C) and Alt is the altitude (m)

RESULTS

Table 1 indicates the maximum, minimum and mean values of indoor air independent variables with respect to MDI concentration in the polyurethane factories. The lowest minimum MDI concentration in all the factories was 93 $\mu g/m^3$ and also the highest of the maximum MDI concentration was 101 $\mu g/m^3$. These values can be considered as high value, compare to NIOSH exposure limit of 50 $\mu g/m^3$. The mean MDI concentration was 96.6 $\mu g/m^3$, the mean indoor relative humidity was 43.7% and the mean dry bulb temperature was 28.7°C. The size of workplace for the five polyurethane factories ranged from 6,300 to 12,500 m^3 and the altitude of factories were from as low as 150 to as high as 1200 m.

It has been summarized and stated in Table 1 that several factories show variable concentration of diisocyanates, with respect to relative humilities of each factory. The highest mean value MDI concentration was 99 $\mu g/m^3$ which corresponds to the highest mean relative humidity of 42.6 % inside of factory M_1.

Table 1: Values of indoor air variables in the MDI polyurethane factories

Factories code Variables	M_1	M_2	M_3	M_4	M_5
MDI concentration (μg/m³) Max	101	98	97	96	95
Min	98	98	96	95	93
Mean	99	98	97	95.6	93.8
Relative Humidity (%), Max	45	45	43	43	43
Min	45	45	43	43	41
Mean	45	45	43	43	42.6
Dry bulb temperature (°C), Max	29	29	29	29	28
Min	29	29	29	28	28
Mean	29	29	29	28.6	28
Mean Dimension (m³)	6300	8600	9800	11200	12500
Mean Altitude (m)	1200	1100	950	890	150

Permissible Exposure Limit: 50 μg/m³ [13]

Table 2: Correlation result for MDI concentration and psychrometric parameters and factory parameters

		MDI (μg/m³)	Rh (%)	Td (°C)	D (m³)	Alt (m)
MDI (μg/m³)	Pearson Correlation	1	0.824(**)	0.826(**)	-0.919(**)	0.795(**)
	Sig. (2-tailed)	.	0.0001	0.0001	0.0001	0.0001
	N	100	100	100	100	100
RH (%)	Pearson Correlation	0.824(**)	1	0.554(**)	-0.838(**)	0.777(**)
	Sig. (2-tailed)	0.0001	.	0.0001	.000	0.0001
	N	100	100	100	100	100
Td (°C)	Pearson Correlation	0.826(**)	0.554(**)	1	-0.714(**)	0.709(**)
	Sig. (2-tailed)	0.0001	0.0001	.	0.0001	0.0001
	N	100	100	100	100	100
D (m³)	Pearson Correlation	-0.919(**)	-0.838(**)	-0.714(**)	1	-0.691(**)
	Sig. (2-tailed)	0.0001	0.0001	0.0001	.	0.0001
	N	100	100	100	100	100
Alt (m)	Pearson Correlation	0.795(**)	0.777(**)	0.709(**)	-0.691(**)	1
	Sig. (2-tailed)	0.0001	0.0001	0.0001	0.0001	.
	N	100	100	100	100	100

** Correlation is significant at the 0.05 level (2-tailed).

Table 3: Regression model summary of MDI

Model	r	R²	Adjusted R²
	0.961	0.924	0.921

Predictors: (Constant), Altitude (m), Dimension of factory (m³), Dry bulb temperature (°C) and Relative humidity (%)

Table 4: Regression model for MDI polyurethane factories factors

Model		Mean Square	F	P value
	Regression	77.411	289.553	0.0001
	Residual	0.267		
	Total			

Predictors: (Constant), Altitude (m), Dimension of factory (m³), Relative humidity (%), Dry bulb temperature (°C), Dependent Variable: MDI concentration (μg/m³)

The data (n=100) of psychrometric parameters (indoor relative humidity and dry bulb temperature) and factory parameters (factory dimension and altitude) in this study were collected and used to predict MDI pollution level. Correlation analysis was carried out after checking the normality assumptions for both variables, Table 2 shows that all parameters are strongly correlated with MDI concentration where $P < 0.05$. The calculated R^2 values for Rh, Td, D and Alt is 0.6789 ($R^2= 0.824^2$), 0.6822 ($R^2=0.826^2$), 0.8445 ($R^2= -0.919^2$) and 0.632 ($R^2= 0.795^2$), respectively.

Since all parameters are strongly correlated, all of them are put in the regression model. Table 3 showed the regression model summary where it can be seen that 92.4% of the MDI concentration can be attributed to any or all the independent variables (relative humidity, dry bulb temperature, dimension and altitude) ($R^2 = 0.924$).

Table 5: Result of regression analysis between MDI concentration and polyurethane indoor air parameters

Model		Coefficients			
		B	SE	t	P value.
	(Constant)	54.320	9.022	6.021	0.0001
	Relative humidity (%)	0.229	0.109	2.099	0.038
	Dry bulb temperature (°C)	1.235	0.201	6.156	0.0001
	Dimension of factory (m^3)	-0.0001	0.0001	-7.767	0.0001
	Altitude (m)	0.001	0.0001	2.366	0.02

Dependent Variable: MDI concentration ($\mu g/m^3$)

Table 6: The collinearity statistical model coefficients

	Coefficients				Collinearity Statistics	
	B	SE	t	P value	Tolerance	VIF
(Constant)	54.32	9.022	6.021	0.0001		
Relative humidity (%)	0.229	0.109	2.099	0.038	0.183	5.459
Dry bulb temperature (°C)	1.235	0.201	6.156	0.0001	0.33	3.033
Dimension factory (m^3)	0.0001	0.0001	-7.767	0.0001	0.195	5.134
Altitude (m)	0.001	0.0001	2.366	0.02	0.267	3.75

Dependent Variable: MDI concentration ($\mu g/m^3$)

The results of the summary imply that all or some of parameters (altitude, dimension of factory, relative humidity and dry bulb temperature) can be significant predictors of MDI concentration in the polyurethane workplaces.

The analysis of variance for MDI concentration in the polyurethane factories showed in Table 4 below. It can be seen from the table that F is 289.553 which is significant at $P < 0.05$. We can conclude that the regression model predicts the concentration level of MDI significantly well.

Since the results of regression model test in Table 4 illustrate that the independent variables are significant predictors of MDI concentration, we can employ equation 1 to stand for the different psychrometric and factory parameters in order to measure the predictive regression correlation between the parameters and MDI concentration.

Table 5 indicates the results of regression analysis and standard error (SE) between MDI concentration and polyurethane indoor air parameters. The factory parameters (factory dimension and altitude) are not significant ($P>0.05$) but relative humidity and dry bulb temperature can be seen to be significant predictors of MDI pollution ($P< 0.05$). This means the size of MDI polyurethane factories and geographical positions of the factories in terms of altitude are not significant where the MDI pollution is concerned and are therefore taken out from the regression model.

The independent variables (relative humidity and dry bulb temperature) were reproduced for the model to find the regression coefficients for MDI pollution in the polyurethane factories. The coefficients with respect to the constant, relative humidity and the dry bulb temperature as well as the collinearity statistics are shown in Table 6.

Multi-co-linearity here refers to linear inter-correlation among psychrometric variables. Collinearity diagnostics was used in this study to find multi-co-linearity between dependent (MDI concentration) and independent variables (relative humidity and dry bulb temperature). If psychrometric variables (relative humidity, dry bulb temperature) correlate highly they are redundant in the same model. Wiley [15] reported that the best regression models are those in which the predictor variables each correlate highly with the dependent (outcome) variable but correlate at most only minimally with each other.

The Variance Inflation Factor (VIF) measures the impact of collinearity among the variables in a regression model. VIF of relative humidity is 5.459 and dry bulb temperature is 3.033, which it is greater than 1. Tolerance lies between zero to one (the VIF is just the reciprocal of tolerance). A value close to zero indicates that a variable is almost a linear combination of the other independent variables. From Table 6 the dry bulb temperature and the relative humidity were not multi-co-linear together. The values of VIF form Table 7 shows the multi-co-linearity and it used to examine the correlations and associations between MDI pollution and relative humidity and dry bulb temperature to detect a high level of association. High bivariate correlations were spotted by running correlations among MDI pollution and relative humidity and dry bulb temperature.

Table 7: The value of model collinearity diagnostics

		Variance Proportions				
Dimension	Eigenvalue	(Constant)	RH (%)	Td (°C)	D(m^3)	Alt (m)
1	4.905	0.001	0.001	0.001	0.001	0.001
2	0.085	0.001	0.001	0.001	0.05	0.08
3	0.01	0.001	0.001	0.001	0.28	0.47
4	0.0001	0.001	0.37	0.22	0.05	0.01
5	2.195E-05	1	0.63	0.78	0.62	0.44

Dependent Variable: MDI Pollution concentration (μg/m^3)

Co-linearity diagnostics was used in this study to find multi-co-linearity between dependent variable (MDI pollution) and independent variables (relative humidity and dry bulb temperature) in the Equation is using collinearity diagnostics result that it detect which variable can be a important variable to make a regression model [15, 16].

Condition indices from Table 7 were used to flag excessive collinearity in the data. If a factor (component) has a high condition index, one looks in the variance proportions column. Whereas, two variables have a variance proportion of 0.5 or higher on a factor with a high condition index these variables have high linear dependence and multi-co-linearity is a problem, it means that the independent variable did not have collinearity to make a linear regression model and each one has a function in the model, with the effect that small data changes or arithmetic errors may translate into very large changes or errors in the regression analysis. Note that, based on the rule of thumb for condition indices (no index over 30) to indicate multi-co-linearity, even when the rules of thumb for tolerance > 0.20 suggested no multi-co-linearity [15].

While, two predictor variables (dimension of factory and altitude) were very small in the model they were eliminated for making a new regression model. In this case, relative humidity and dry bulb temperature were significantly contributed to the model after eliminating the above variables (dimension of factory and altitude). The overall model fits the data well, but neither the altitude nor the dimension of factory made a significant contribution when it was incorporated into the model last. When this happened, multi-co-linearity is presented.

Replace Y, X_1 and X_2 with MDI, Rh (relative humidity) and Td (dry bulb temperature), respectively. By substituting the relevant coefficients from Table 6, into Equation 1, written as follows:

$$MDI = 54.32 + 0.229Rh + 1.235Td \qquad (2)$$

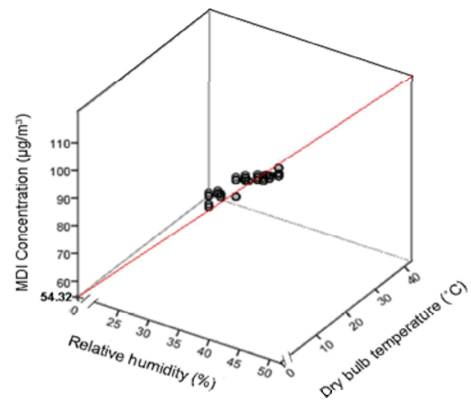

Fig. 1: Relationship between MDI concentration and psychrometric factors

Based on Table 7, the relative humidity has 63% contribution on the model linear regression and moreover the dry bulb temperature has 78% contribution on the model linear regression (equation 2) and it has influenced individually into linear regression model and each dependent variables have separately contribution and both of them is necessary to put into the linear regression model of 4 as predictors.

The relative humidity and dry bulb temperature affects on diisocyanates pollutant generation facility and emitted diisocyanates in the work places quickly. In other words, dry bulb temperature affected on diisocyanates pollutant generation speed, the volatility of the isocyanates emission into workplaces depend on temperature and speed of the reaction [15].

Figure 1 shows the relationship between MDI concentration and psychrometric parameters (relative humidity and dry bulb temperature) in the five polyurethane factories (Equation 2).

Both indoor air relative humidity and dry bulb temperature are significantly contributing to the variability of the MDI concentration ($R^2 = 0.924$) and both factors also show a straight positive relationship with the MDI concentration. This means that as the indoor relative humidity or the dry bulb temperature increases, the MDI concentration also increases. Equation 2 also shown in Figure 1 suggests that the average background MDI concentration was about 54.32 μg/m^3 as indicated by the value of the constant in the regression equation. Such transformation requires a complete understanding of how environmental and other factors (e.g. air velocity, temperature, humidity) can influence emissions [17]. The knowledge is also essential for reliable assessment of the impact of building materials on indoor air quality.

DISCUSSION

In this study the indoor temperatures of the factories ranged from 23 to 33°C. The linear relationship between temperature and diisocyanate concentration is acceptable since the indoor temperatures were not greater than 40°C where exponential increase of isocyanate emission could occur.

In a study of spray application of isocyanate paints to a car body shop at UK petrol stations showed that airborne isocyanate concentrations were below the permissible exposure limit; [18] in their study relative humidity and indoor temperature were the effective factors on diisocyanates emission. Although indoor temperatures were not cited in their study as a straight effective factor given the geographical location of the study based on psychrometric condition.

The effect of relative humidity on the curing and dielectric properties was assessed in the USA polyurethane factories [19]. They have reported that 87% relative humidity (Rh) as compared to 43.7% relative humidity of the diisocyanates workplaces was a perceptible effect. The water vapor during the curing process in polyurethane process was strongly influenced by the electromagnetic properties of the polyurea/polyurethane-based composites, while evidenced by the significant difference in the real relative permittivity of samples cured in different Rh environments. This difference was caused primarily by water uptake into the polymer matrix. The Rh alters the dielectric properties of the composite material due to its strong polar nature and high value of real relative permittivity.

The range of Rh was in the range of 41 to 45% in this study. The standardized beta coefficient in the MDI regression for relative humidity was 0.229 which is lower than that of the coefficient for temperature (1.235) as shown previously in Table 5.7. The working range for Rh in this study is lower than that reported by Abram and Bowler (2005) for noticeable effects (87% Rh), hence the effects of Rh is expected to be not as significant as to the effects of temperature [20].

Another study was done for the effects of relative humidity on isocyanate concentration; they found that reactions of isocyanate groups with OH groups during cross-linking are inversely proportional to the relative humidity of the environment. The presence of competing reactions, such as between water and isocyanate, hinder the degree of cross-linking between them expressed by Ludwig and Urban [19].

During paint spraying, the low volatility, partially cured MDI become airborne as aerosols while the unreacted monomeric isocyanates vaporize [21]. The high indoor temperatures of the workplaces that located the MDI polyurethane factories experienced the enhanced vaporization of the diisocyanates. Furthermore, the emission of diisocyanates in the workplaces is likely to be accelerated at the elevated temperatures and high humidity [22].

The relationship between psychrometric factors such as indoor temperature, relative humidity were pull out from normal gas law related to gas emission behavior in the workplaces that it depended to reaction of isocyanates [23]. The result of this study showed diisocyanates had a relationship to altitude. Altitude has a reverse relation with air pressure this can be ascribed to the higher volatility of isocyanate; mentioned to this relationship as well.

The influence of relative humidity on the rate of isocyanate pollution in the polyurethane workplaces was investigated via indoor humidity assessment. The effect of relative humidity (Rh) ranging from 41 to 45% on indoor air pollution was studied. The results indicate that the rate of isocyanate concentration in the workplaces is directly proportional to the Rh. The results are discussed in terms of the reactions which occur between water and isocyanate, as well as the plasticization effects of water and solvent molecules [24].

In the current study the mean isocyanate concentration was 96.6 μg/m^3 (0.097 mg/m^3). This is comparable to a study of Iranian automobile manufacturing company, he reported for a geometric mean concentration between 27.73 and 34.53 μg/m^3 methylene diphenyl diisocyanates [24].

CONCLUSION

The results of air monitoring in all the five Iranian polyurethane factories showed that all MDI concentration values can be considered high in comparison with NIOSH exposure limit of 50 μg/m^3. The MDI concentration ranged from 93 to 101 μg/m^3 with a mean MDI concentration of 96.6μg/m^3.

Both indoor air relative humidity and temperature have significantly contributed to the variability of the MDI concentration (R^2=0.924) and both factors also showed a straight relationship with the MDI concentration. The size of the factories and altitude of the factories did not show significant predictors of MDI concentration level in the factories. MDI was found through multiple linear regressions to relate relative humidity and indoor air temperature according to equation 2.

The background MDI concentration was about 54.32 μg/m^3 as indicated by the value of the constant in the regression equation.

The current work admittedly has limitations but may be a useful initial tool in estimating possible MDI pollution situation in the polyurethane workplaces based on simple psychrometric factors (indoor air temperature and relative humidity). It can serve as a basis of future evaluation and intervention efforts to reduce the workers to isocyanate exposure.

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