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INFLUENCE OF UREA CONCENTRATION ON REFRACTIVE INDEX OF ADBLUE FLUID EVALUATED BY REGRESSION ANALYSIS

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Abstract

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The article deals with the influence urea concentration in the AdBlue fluid on the refractive index. The AdBlue fluid is an aqueous solution of urea and demineralized water. It is used as a reducing agent for SCR (Selective Catalytic Reduction) system. Due to temperature fluctuation of AdBlue during the measurement of refractive index, the multi-dimensional linear regression had to be used to determine the effect of the two factors – concentration and temperature. This article describes in detail the individual steps of the regression model construction done using the so-called regression triplet. The task of this method was to create a regression model which describes the influence urea concentration and small changes in temperature on refractive index of AdBlue fluid. As the results of the multi-dimensional regression analysis show, the temperature factor is statistically insignificant because of small range of temperature fluctuation during measurement, and thus only the urea concentration in the fluid had the major effect on the refractive index.

Keywords: refractive index, multi-dimensional regression analysis, regression triplet, regression model, method of least squares

INTRODUCTION

Emissions of nitrogen oxides belong to the most widespread harmful substances in the exhaust gas of a diesel engine (Karavalakis *et al.*, 2012). One of the systems used for their reduction is the SCR (Selective Catalytic Reduction) system (Radivojevic, 1998). The basic element of this system is a reduction catalyst wherein the nitrogen oxides NO_x are converted into nitrogen N_2 and water H_2O using a chemical reaction of the reducing agent – ammonia NH_3. For the reduction of nitrogen oxides is therefore necessary to inject a sufficient amount of reducing agent depending on operating conditions. The reducing agent is conveyed into the catalyst in the form of urea with demineralized water. The mixture with demineralized water contains 32.5% of urea. The decomposition of urea solution into ammonia is then carried out in an upstream hydrolytic catalyst (Wiesche, 2007). The urea and water solution is branded AdBlue in Europe, DEF (Diesel Exhaust Fluid) in North America. The reason why pure ammonia is not used is its high toxicity and negative impact on both human health and the environment.

Composition and quality of aqueous urea solution is specified in the ISO 22241-1 standard. It gives the urea content, density, or refractive index. It also specifies the maximum allowed amounts of substances that may be contained in the fluid (e.g. calcium, sodium, aldehydes, etc.).

As already mentioned, in order to reduce NO_x in the SCR catalyst it is necessary to use a reducing agent. The use of AdBlue fluid thus increases the operating costs. For this reason, the practice of AdBlue fluid additionally diluted with water either normal or demineralized can be encountered. Using AdBlue fluid with lower urea concentration consequently leads to a reduction in conversion efficiency and in addition, upon dilution with normal water it leads to injector and catalyst clogging with limescale.

Assessment of the AdBlue fluid quality can be performed by control measurements of the urea concentration by measuring its density or refractive index using a refractometer.

In most cases, the measurement of the refractive index is based on limit angle of refraction measurement. Refractive index is considered as characteristic quantity of many substances that is used for their identification. Measurement of the refractive index using a refractometer is especially advantageous due to low consumption of tested sample and rapid, simple and accurate measurement (Avison, 1989). In the automotive industry, the refractometers are very often used e.g. for checks of the cooling liquids, battery charge status, brake fluid quality etc. (Kalous, 1987; Ryan, 2014).

The article deals with the use of regression analysis for the construction of a regression model in order to verify the relationship between refractive index and urea concentration. The regression analysis is a method to investigate the relationships between variables (Chatterjee and Hadi, 2006).

MATERIAL AND METHODS

Measurements were performed on a sample of fluid which meets the ISO 22241-1 standard. Selected parameters of AdBlue fluid given by the ISO 22241-1 standard are shown in Tab. I.

Measurement of refractive index at corresponding temperature has been performed using the ATAGO PAL-RI manual refractometer. The refractometer has been equipped with a digital thermometer. Technical specification of the refractometer is shown in Tab. II. Demineralized water has been used for calibration of the instrument.

Actual measuring of refractive index at corresponding temperature of the fluid has been repeated several times to minimize measurement errors. First measurements have been performed on a sample of undiluted AdBlue fluid. The sample has been then diluted with normal water, calculating the current concentration. The measurements the aforementioned values have been performed during the gradual dilution of the sample. Dilution of AdBlue fluid has been conducted up to 13% urea concentration in the fluid. The measurement on pure demineralized water used in the measurement has been performed in the last phase.

RESULTS AND DISCUSSION

The refractive index upon dilution of AdBlue fluid by demineralized water has been monitored in the experiment. Due to temperature fluctuation of AdBlue during the measurement (from 24.6 °C to 26.8 °C), the multi-dimensional linear regression had to be used to determine the effect of the two factors. As reported by Kalous (1987) when measuring the refractive index of the liquid the temperature of the fluid being measured is necessary to be taken into account, as in the case of

I: *Selected parameters of AdBlue meeting standard ISO 22241-1*

Parameter	Specification
Urea content	32.5 ± 0.7% mass content
Density (20 °C)	1087–1093 kg.m^{-3}
Refractive index	1.3814–1.3843

II: *Technical specifications of refractometer ATAGO – PAL RI*

Parameter	Specification
Measurement range	1.3305–1.5284
Resolution	0.0001
Measurement accuracy	± 0.0003
Automatic temperature compensation	NO

a temperature increase of 1 °C the refractive index decreases by about 0.0003 to 0.0008 units.

Graphic form of measured values is shown in Fig. 1.

The multi-dimensional regression analysis has been used to create a regression model that describes the effect of urea concentration at corresponding temperature of the sample analyzed on its refractive index. The Statistica 12, QC.Expert 3.3, and NCSS 9 software has been used for exploratory data analysis and construction of the regression model itself. Multiple software tools have been used mainly to verify the calculation accuracy.

At construction of the regression model, the least squares method is used very often. The least squares method provides satisfactory estimates of regression parameters, but only if all assumptions about the data and the regression model are met (Meloun *et al.*, 2002).

Basic assumptions about the data have been verified prior to multi-dimensional regression analysis itself. It was found by the use of appropriate diagnostic tools (Shapiro-Wilk W-test, quantile-quantile plot, boxplot, etc.) that the initial data satisfy the basic assumptions and can be used to construct a regression model.

The regression model construction procedure consists of model suggestion and subsequent regression diagnostics (Meloun and Militký, 2011). The suggested regression model had the following form:

$$y = \beta_0 + \beta_1 \cdot x_1 + \beta_2 \cdot x_2, \qquad (1)$$

where

y................ refractive index [-],

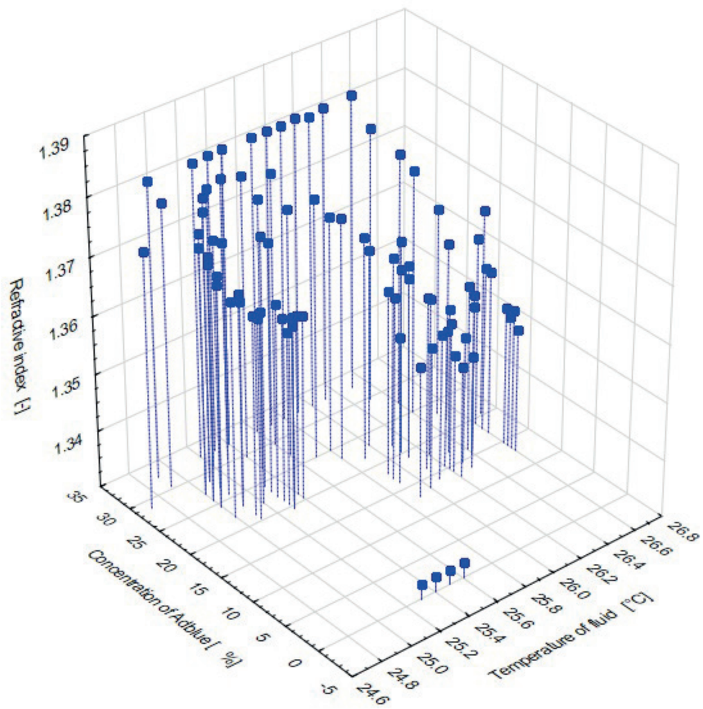
$\beta_0, \beta_1, \beta_2$...... regression parameters,

x_1.............. concentration of urea [%],

x_2................. temperature [°C].

In the first step, the best estimates of the regression parameters have been found using the least squares method. The Student's t-test used according to the eq. (2) has verified whether the individual regression coefficients are statistically significant,

$$t_{\alpha_2;n-m} < |(b_j - \beta_j)/s(b_j)|, \qquad (2)$$



1: *Measured values of refractive indexes at relevant temperatures*

III: *Estimation of parameters with results their statistical significance verified by t-test and with confidence limits of regression parameters*

Independent variable	Regression Coefficient bj	Standard error $s(b_j)$	T-Statistic to Test H0: $\beta_j = 0$	Prob. level	Lower 95.0% Conf. Limit of β_j	Upper 95.0% Conf. Limit of β_j
Intercept	1.338589	0.0091956	145.569	$p < 0.001$	1.32341	1.356837
Concentration of AdBlue	0.0015232	$2.11791.10^{-5}$	71.920	$p < 0.001$	0.0014812	0.0015652
Temperature	–0.0002353	0.000355	–0.663	0.5089	–0.00094	0.0004691

where

n .... number of values,
m................... number of variables,
b_j................ estimations of regression parameters,
$s(b_j)$.............. estimation of regression parameter standard error,
β_j................... jth regression parameter.

Test proved that the β_2 parameter is statistically insignificant. Values of the estimated regression parameters with Student's t-test results are shown in Tab. III.

Also the calculation of the following basic static characteristics of regression has been conducted in this step (Kumbár and Dostál, 2014):

- coefficient of correlation R:
- coefficient of determination R^2, which represents the percentage of variability explained by the model.

According to Meloun and Militký (2001), one of the most efficient test criterion for testing regression model quality is mean quadratic error of prediction (MEP) and Akaike information criterion (AIC) – these criteria are decisive for distinguishing among several proposed models, optimal model reaches minimum value of MEP and AIC. Mean error of prediction is defined by equations (3):

$$MEP = \frac{\sum_{i=1}^{n}\left(y_i - x_i^T b_{(i)}\right)^2}{n}, \quad (3)$$

where

x_i.................... ith row of matrix X,
X .... a fixed $n \times m$ design regressors matrix of explanatory (independent) variables,
$b(i)$................ the estimate of regression parameters when all points except the ith one were used and
x_i................ the ith row of matrix X (Meloun and Militký, 2001).

Akaike information criterion is calculated by equations (4):

$$AIC = n \cdot \ln\left(\frac{\sum_{i=1}^{n}\left(y_i - \sum_{j=0}^{m} x_{ij} b_j\right)^2}{n}\right) + 2m, \quad (4)$$

where
n .... number of values,
m .... number of parameters (variables),
x_{ij} .... independent variable ith row and jth column.

Mean quadratic error of prediction can be used to express the predicted determination coefficient (coefficient represents predictive ability of the model). Predicted coefficient of determination is calculated by equations (5):

$$R_p^2 = 1 - \frac{n \cdot MEP}{\sum_{i=1}^{n} y_i^2 - n \cdot \bar{y}^2}. \quad (5)$$

The regression diagnostics followed. It includes means for interactive analysis of data, model, and method, i.e. the components of so-called regression triplet Data criticism has been performed using the analysis of residues, Atkinson distance, using the plots indicating influential points (Pregibon plot, Williams plot) and using rankit plots – see Fig. 2.

One outlier has been detected using the data criticism. As the plots show, the point 87 affects the accuracy of the regression model and the normality of concerned residues distribution the most.

The detection of influential points has been followed by the suggested model criticism. The suggested model criticism has been conducted using partial regression and especially partial residual plots. Fig. 3 and Fig. 4 show the partial residual plots for each variable.

Fig. 3 shows a clear linear dependence of the independent variable "urea concentration" (x_1). In contrast, the independent variable "temperature" (x_2) exhibits high dispersion (Fig. 4). It is not a linear dependency and therefore its presence is insignificant in the suggested model. This is also confirmed by the results of Student's t-test for statistical significance of individual independent variables.

Method criticism is the last step of the regression triplet. Method criticism is conducted using several statistical tests (Meloun and Militký, 2011)

- Fisher-Snedecor test of regression model significance.
- Scott criterion of multi-collinearity to verify of model correctness.
- Cook-Weisberg test of residues heteroscedasticity (constancy of variance).
- Jarque-Berra normality test of residues.
- Wald test and Durbin-Watson test of autocorrelation.
- Test to determine whether the trend is not in residues.

Based on results of these tests, our calculated model meets all requirements for used method of least squares.

The final step after removal of the outliers and irrelevant variables is the refined model construction. After removal of independent variable x_2 (temperature), the multi-dimensional model has been simplified to a simple one-dimensional linear dependence given by the following equation:

$$y = \beta_0 + \beta_1 \cdot x_1. \quad (6)$$

Repeated estimation of individual regression parameters β_0 and β_1 using the least squares method followed. The results are shown in Tab. IV. The results of the static characteristics of regression are shown in Tab. V.

The high value of the correlation coefficient indicates that the suggested linear regression model is statistically significant, which has been subsequently confirmed also by Fisher-Snedecor test for the model significance. The determination coefficient shows that all the points highly correspond with the model. For this reason it is not necessary to use a model with e.g. second-stage transformation.

Construction of the refined regression model led to the calculation of an equation which describes the relationship between urea concentration in AdBlue fluid and refractive index with high accuracy. Based on analyzes preformed above, the influence of examined sample temperature can be neglected. The calculated equation then has the following resulting form (in parentheses there are estimates of the standard deviations of given parameters):

$$y = 1.332477(0.0004618) + 0.0015231(2.02274 \cdot 10^{-5})x_1. \quad (7)$$

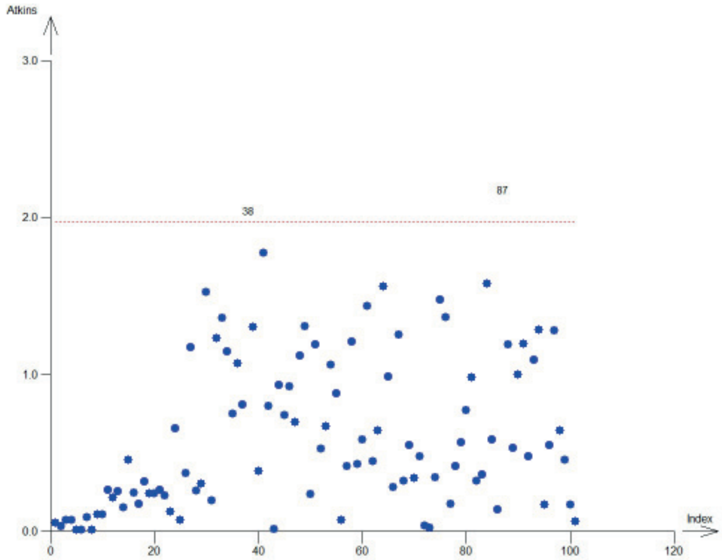
As the analyses show, the small range of temperature fluctuation did not affect the refractive

V: *Static characteristics of regression*

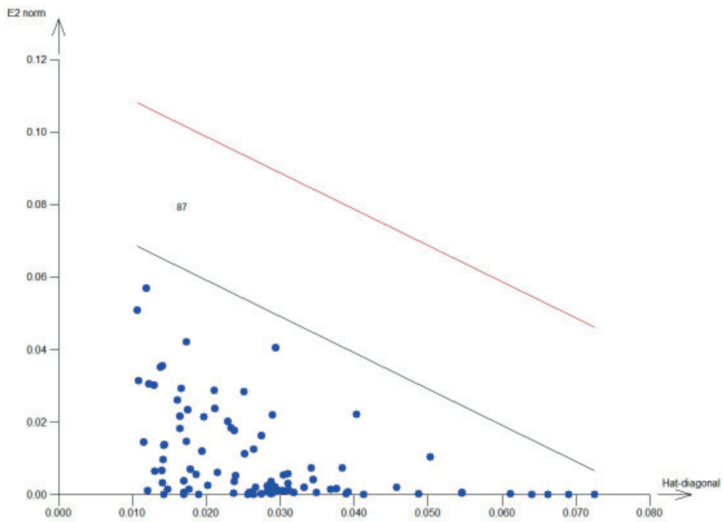
Coefficient of correlation R	0.99147
Coefficient of determination R^2	0.98301
Mean error of prediction MEP	$3.476 \cdot 10^{-6}$
Akaike information criterion AIC	–1255.44
Predicted coefficient of determination R^2_P	0.96547

IV: *Estimation of parameters with results their statistical significance verified by t-test and with confidence limits of regression parameters at refined regression model construction*

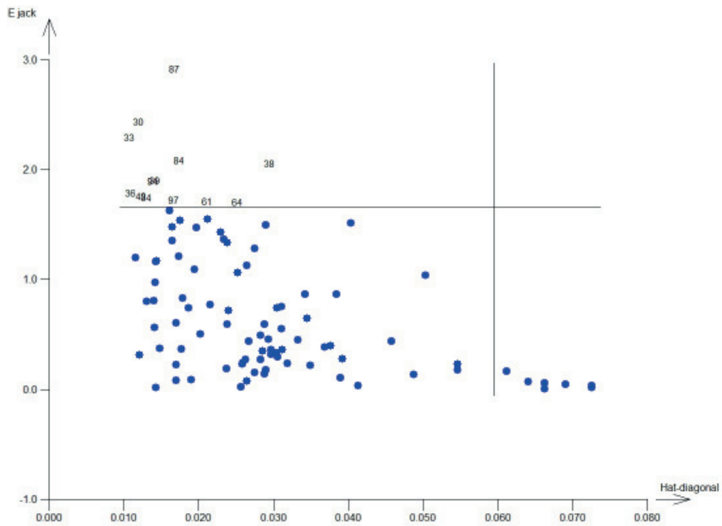
Independent variable	Regression Coefficient b_j	Standard error $s(b_j)$	T-Statistic to Test H0: $\beta_j = 0$	Prob. level	Lower 95.0% Conf. Limit of β_j	Upper 95.0% Conf. Limit of β_j
Intercept	1.332477	0.0004618	2885.528	$p < 0.001$	1.331561	1.333394
Concentration of AdBlue	0.0015231	$2.02274 \cdot 10^{-5}$	75.301	$p < 0.001$	0.001483	0.0015633



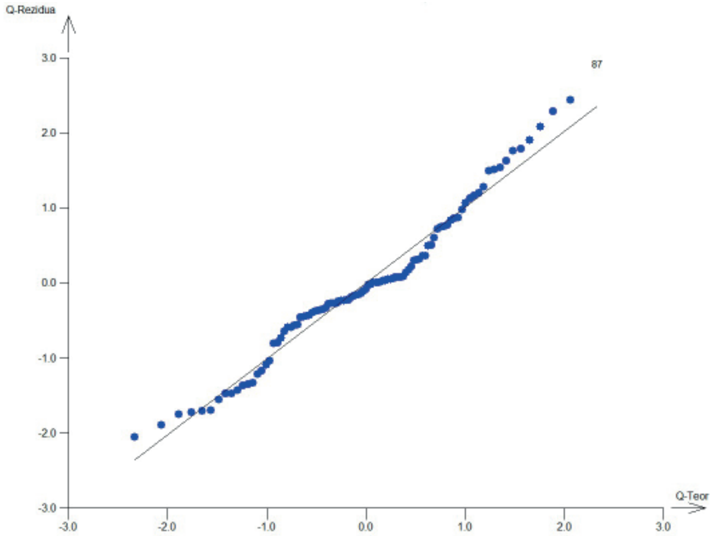
2a: *Atkinson distance plot*



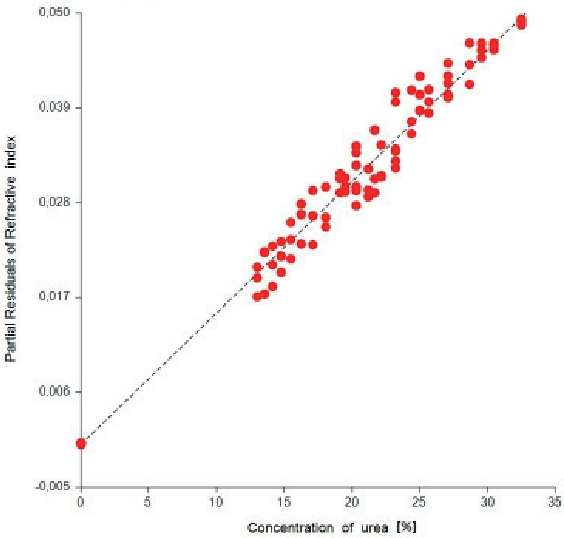
2b: *Pregibon plot*



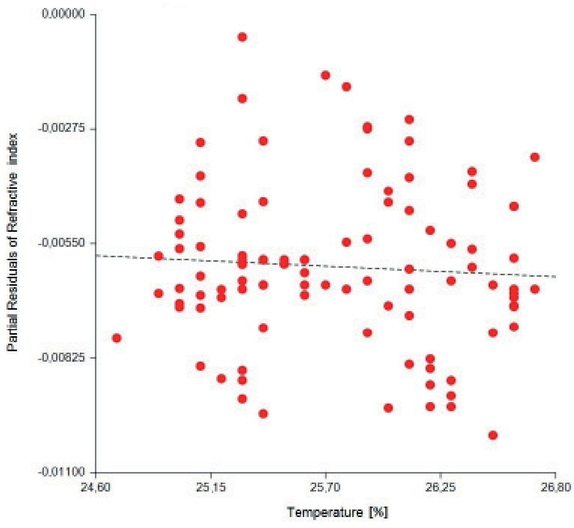
2c: *Williams plot*



2d: *Rankit plot of Jackknife residues*



3: *Partial Residuals of Refractive index vs. Concentration of urea*



4: *Partial Residuals of Refractive index vs. Temperature* index of the fluid statistically significantly and the major effect has only the urea concentration in AdBlue fluid.

Besides the obtained results of experimental measurements, this article has another objective to describe in detail the process of multi-dimensional regression model construction using the so-called regression triplet utilizing modern statistical software.

CONCLUSION

One of the systems used for reduction of nitrogen oxides emissions is the SCR (Selective Catalytic Reduction) system The basic element of this system is a reduction catalyst wherein the nitrogen oxides NOx are converted into nitrogen N_2 and water H_2O using a chemical reaction of the reducing agent – ammonia NH_3. The reducing agent is conveyed into the catalyst in the form of urea mixed with demineralized water. The mixture with demineralized water contains 32.5% of urea. The urea and water solution is branded AdBlue in Europe. The use of AdBlue fluid increases the operating costs. For this reason, the practice of AdBlue fluid additionally diluted with water either normal or demineralized can be encountered. Using AdBlue fluid with lower urea concentration consequently leads to a reduction in conversion efficiency and in addition, upon dilution with normal water it leads to injector and catalyst clogging with limescale.

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