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ANALYSIS OF PETROCHEMICAL FEEDSTOCK AND PRODUCTS BY NEAR INFRARED SPECTROMETRY

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Abstract

Near infrared spectrometry (NIR) is a modern analytical method which is successfully used in the area of control and processing in the chemical, food and pharmaceutical industries. This method presents a technique which increases effectiveness, accuracy and safety of results.
A correlation between variables is found by use of special models which are not associated directly. Then it is possible to predict a result of mechanical properties of petrochemical products.
This article focuses on the determination of type, content and properties of hydrocarbon feedstock which are contained in straight-run gasoline and hydrocracking vacuum distillates. These fractions present basic petrochemical feedstock for a steam cracking unit. NIR application was applied for the determination of ethylene contained in polypropylene impact copolymers.

***Keywords**: NIR spectrometry, BMCI, density, co-polymer, primary gasoline, hydrocracking vacuum distillates.*

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1. Introduction

NIR spectrometry is modern analytical method used for qualitative and quantitative characterization of structure compounds. This method is used in many fields [1-5]. It enables fast quality control. Its big advantages are a rate of the determination, accuracy, reliability and low demands for an operator. This article shows applications of NIR spectrometry for chosen petrochemical feedstock and products, especially feedstock for steam cracking unit. The determination of ethylene total amount demonstrates a usefulness of NIR spectrometry. The amount of ethylene is measured in block-copolymers of polypropylene without a pre-treatment.

The method was used for the determination of basic refinery-petrochemical characterization of feedstock. Basic feedstocks of steam cracking unit are straight-run gasoline (PRIMBI) and hydrocracking vacuum distillates (HCVD). Bureau of mind correlation index (BMCI) and density were used for characterization of HCVD. Primary gasoline was characterized by its type.

Correlation models were created for these characterizations and verified by many groups of samples in long term. The goal of the applications was to substitute very time consuming methods by more effective NIR spectroscopy while keeping the necessary accuracy and reliability of the obtained results.

2. Experiments

The model was created according to data obtained from Nicolet 6700 FT-IR device supplied by Thermo Scientific. System contained InGaSe detector. Measurement conditions were 50 scans with resolution 4 for each spectrum. Measurement was carried out five times by an immersion cell HELMA, 5 mm and then the averaged spectrum was used in the model. For the measurement OMNIC software was used and TQ Analyst software was used for the model creation.

3. Result and discussion

The determination of type for straight-run gasoline is very important for its qualitative evaluation. There were determined five types in gasoline – alkanes, isoalkanes, naphthenes, olefins and aromatic hydrocarbons determination. The correlation model was developed for each type group.

Straight-run gasoline samples were used as standards after analysis by GC, which was used as reference method. Considerable time consumption is disadvantage for GC in the determination of each compound in a group. The results were summarized for all compounds in the group. The distinction of each compound was not necessary. Figure 1 shows an NIR model which correlates the content of aromatic hydrocarbons in straight-run gasoline by GC and NIR methods. The model is characterized by basic parameters – Root mean square error of cross-validation (RMSECV) and correlation index. RMSECV is a basic value characterizing the error of a model. This error cannot be lower than the error of the reference method.

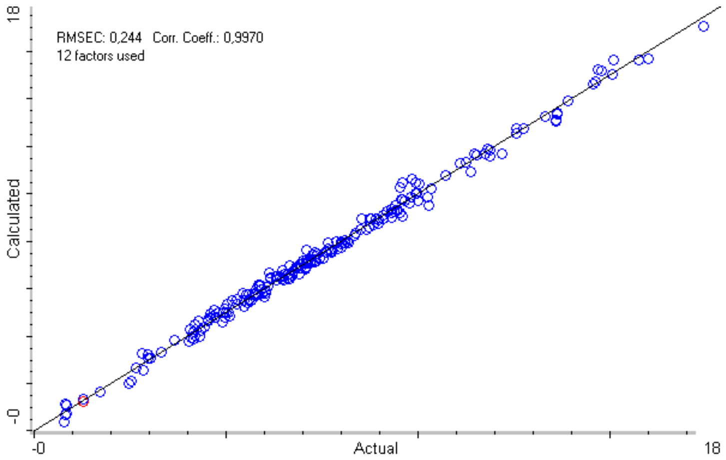

Figure 1 NIR model for determination of aromatic hydrocarbons in straight-run gasoline.

The correlation index presents a satisfactory conformity among measured values and values calculated by chemometric algorithm. Used chemometric algorithm was PLS (partial least squares). The model range of aromatic hydrocarbons was 0.7-18% (w/w). This model contained 210 standards where the value RMSECV was 0.35% (w/w). In this case very good correlation was reached after the application of the described chemometric algorithm which enabled the implementation of the model into routine use. Further 4 models of alkanes, isoalkanes, naphthenes and olefins were developed by the same treatment.

The second important feedstock for a steam cracking unit is presented by hydrocracking vacuum distillates (HCVD). In this case properties of HCVD are measured. These values are a correlation of density and BMCI (Bureau of Mines Correlation Index). Both relate to the chemical composition of the samples. Figure 2 shows the NIR model for the correlation of HCVD density and NIR spectra. An instrumental densitometry was selected as reference method to this purpose. Root mean square error of cross-validation (RMSECV) and correlation index are parameters characterizing NIR model. This model was based on 192 standards in the range 847-862 kg/m3. The RMSECV was 0.65 kg/m3. This number is considered to be an acceptable error of measurement.

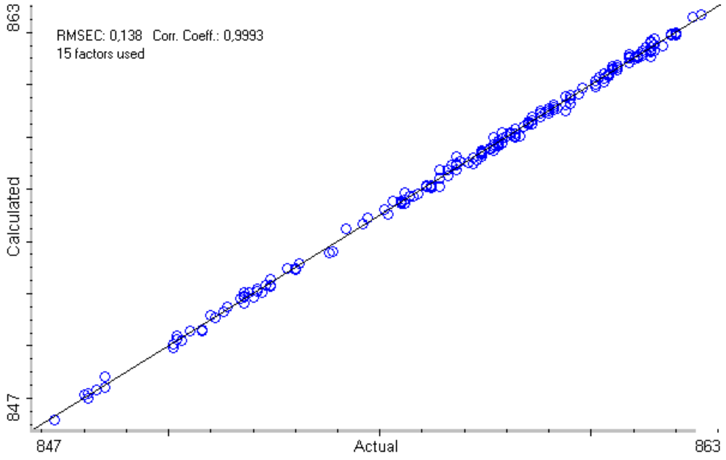

Figure 2 NIR model for density determination of hydrocracking vacuum distillates (HCVD).

This model was verified many times before its implementation for external verification. Figure 3 shows the verification of conformity with densities which were measured by instrumental densitometry. These samples were chosen randomly.

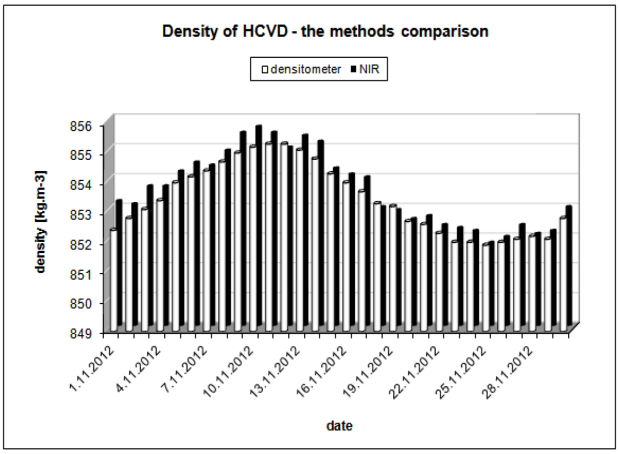

Fig. 3 Comparison of measured values of HCVD density by NIR spectrometry and instrumental densitometry.

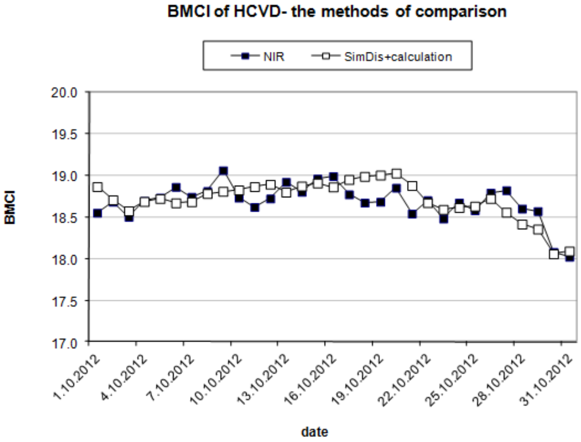

Fig. 4 Comparison of measured values BMCI by NIR spectrometry and SIMDIS.

The next model was developed to correlate the BMCI (Bureau of mines correlation index) in the same way as density of HCVD. BMCI is an empirical parameter which is calculated from the average boiling point of HCVD and density at 20°C.

Simulated distillation (SIMDIS) and densitometry were used as reference methods to determine boiling point and density, respectively. Liquid samples were measured at 80°C by immersion cell. This was similar to the measurement of straight-run gasoline. The RMSECV value was 0.37 in the BMCI range 15-28 and 102 calibration standards were used. The Figure 4 shows a verification of randomly chosen samples. This graph compares two curves, the first shows an evaluation of randomly chosen samples by NIR model and the second illustrates the calculated value of BMCI from SIMDIS and densitometer which is the conventional method. Table 1 contains basic statistical values related to Figure 4. Both models are suitable for routine evaluation for the quality of HCVD and the control and processing of the steam cracking unit.

Table 1 Statistical parameters related to Figure 4.

parameter	BMCI	
	NIR	SIMDIS
Average	18.68	18.71
Median	18.70	18.72
Maximum	19.06	19.03
Minimum	18.02	18.06
Variance	0.05	0.05
SMODCH	0.22	0.23

The final NIR model was developed for the determination of structural content of block co-polymers in polypropylene. The block co-polymer was ethylene (C2).

Polymer powders which contain different concentrations of ethylene in polypropylene were measured. In this case the NIR spectrometer was used to measure an interflection. Each powder sample was measured in a rotating cuvette. ^{13}C NMR was used as reference method. Samples measurements by the FTIR method were preferred for the verification of sample groups because ^{13}C NMR method is not suitable for routine analyses and is very expensive. Samples were analyzed as a thin film of polymer by FTIR.

The new developed model is given in the Figure 5. This model predicts total content of ethylene in polypropylene. RMSECV was 0.30% total content of ethylene (C2) in the range 0.05-16.3 % C2. The correlation index was 1,0000 when 52 calibration standards were used. Results of this verification are listed in the Figure 6. Each type of co-polymer PE in PP differs on the content of total ethylene.

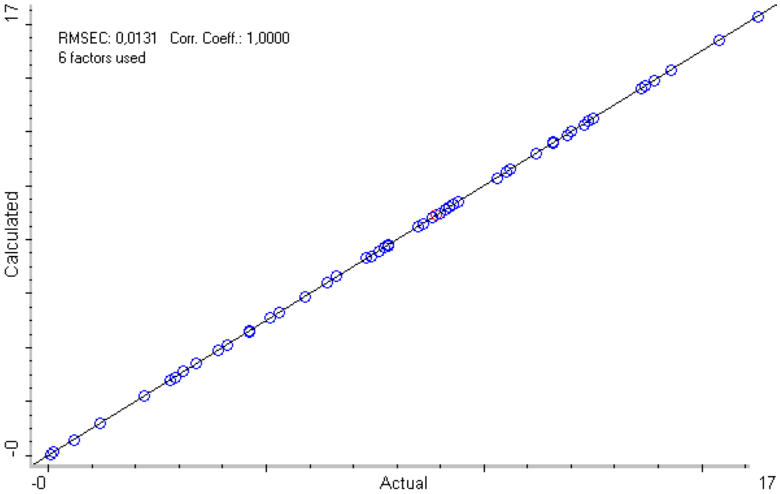

Figure 5 NIR model for the determination ethylene in propylene.

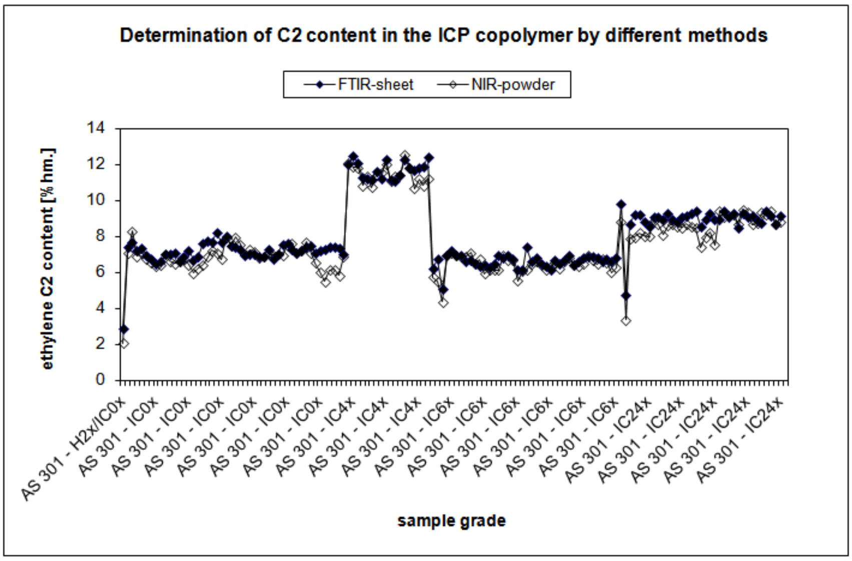

Figure 6: Comparison of results for the determination of ethylene in co-polymers by the method NIR and FTIR.

4. Conclusion

NIR spectrometry is very fast, simple and efficient analytical method. It is very often used in experimental condition. One of its advantages is the fast rate of analysis. The second advantage is that analysis can be performed without sample pre-treatment. Therefore this method presents a reliable and accurate alternative to the given reference methods. The model has to include a sufficient amount of calibration standards without vacancies. The error of prediction, cross-validation and calibration should be a close model to work correctly.

Acknowledgments

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List of symbols

NIR	*Near InfraRed spectrometry*
PRIMBI	*Straight-run gasoline*
HCVD	*Hydrocracking Vacuum Distillates*
BMCI	*Bureau of Mines Correlation Index*
FTIR	*Fourier Transform InfraRed spectrometry*
RMSECV	*Root Mean Square Error of Cross-Validation*
SIMDIS	*Simulated distillation*
C2	*ethylene*
^{13}C *NMR*	*Carbon Nuclear Magnetic Resonance spectrometry*

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