Near infrared spectroscopy applied to paraffin hydroisomerisation process control: a feasibility study

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Introduction

Near infrared (NIR) spectroscopy, combined with multivariate data analysis, offers many interesting perspectives in the advanced control of petroleum processes due to high speed computations and reliability.[1–4] Moreover, the use of fibre optics allows it to be used easily on-line.

The basis of these processes involves establishing relationships (models) between absorbances in the NIR region and chemical–physical characteristics of the products.

The most studied application in the petroleum field is gasoline and gasoil quality prediction, mainly for efficient control of fuel blending plants, but applications to other petroleum products and processes have also been described.[5–8]

In this work, the NIR/partial least squares (PLS) technique is applied to estimate a branching factor of products resulting from the hydroisomerisation of n-paraffins. The predictive PLS model has been calibrated with standard model compounds.

Experimental section

Calibration set

The calibration set consisted of 19 model compounds, representative of the expected variations in the hydromerisation products composition:

- linear alkanes: pentane, hexane, heptane, octane, nonane, decane, tetradecane, hexadecane, octacosane and dotriacontane
- branched alkanes: squalane, 2,6,10,14-tetramethylpentadecane, 2,3-dimethylbutane, 2-methylbutane and isoctane
- cyclic alkanes: cyclohexane, decahydronaphtalene-*cis*, tertbutylcyclohexane and n-butylcyclohexane

Hydroisomerisation products

The products from the hydroisomerisation process bench-scale microreactor, were sampled at increasing conversion of the feedstock, a linear paraffin (n-hexadecane) (Samples 1–10). The amount of unreacted n-C_{16} in the products was determined by gas chromatography.

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Spectroscopy

Near infrared transmission spectra were recorded between 1100 nm and 2250 nm at 2 nm resolution with a Guided Wave Model 260 spectrometer interfaced to a Compaq microcomputer. The spectrometer was configured with a tungsten–halogen lamp as the light source, a 300 line mm^{-1} diffraction grating and a PbS detector. Two Guided Wave 2.5 m long optical fibres connected the spectrometer to the measurement cell holder. A glass cell, with an optical pathlength of 10 mm, was used to record the spectra of the model compounds in 20%(w / w) carbon tetrachloride solutions. A 2 mm pathlength glass cell was used for the pure liquid samples. Four spectra were recorded for each sample and averaged. The reference spectrum was taken in air before each measurement. The spectra were baseline corrected, using the absorbance minimum values at 1320 nm and 1570 nm for offset and tilting correction. Then, they were normalised between 1100 and 2250 nm according to the mean normalisation method. The spectra of n-heptane, 2,3-dimethylbutane, n-butylcyclohexane and one sample are presented in Figure 1.

Prediction model

The partial least squares (PLS) method (PLS2 algorithm) was used to compute predictive models of the molar fractions of the methyl (f_{CH3}), methylene (f_{CH2}) and methine (f_{CH}) groups in the alkanes. The UNSCRAMBLER modelling program, developed by CAMO (Trondheim, Norway), was used to run the PLS analysis.

The absorbance values of the NIR spectra for the $n = 19$ calibration samples were used as independent variables (X). The molar fractions of CH_3, CH_2 and CH were the dependent variables (Y). The relationship between the NIR spectrum of a sample and the molar fraction of the groups is given by the equation:

$$[f_{CH^*}] = \sum_{i=1}^{n} [Bi,_{CH^*} \bullet A(\lambda_i)]$$

where $A(\lambda_i)$ is the absorbance at wavelength λ_i and the B_{i,CH^*} are the regression coefficients calculated for the CH_* group (CH_3, CH_2 or CH) with the PLS2 algorithm. The predictive ability of the model was evaluated through the standard deviation of the error of prediction (*SDEP*) value , defined as follows:[9]

$$SDEP = \sqrt{\frac{\sum_{i=1}^{n} (Y_{i,ref} - Y_{i,calc})^2}{n-1}}$$

where $Y_{i,ref}$ and $Y_{i,calc}$ are, respectively, the actual and the calculated molar fraction of the CH_* group in the i^{th} sample. The calculated Y were obtained by leave-one-out (LOO) and by grouped cross-validation methods.

Results and discussion

The group of overlapping bands at low wavelengths (1150–1230 nm) in the NIR spectra is assigned to the second overtone of the fundamental stretching vibrations.[10–11] In particular, the methyl absorption is around 1190 nm and methylene absorption around 1210 nm. The complex band between 1350 and 1460 nm is the sum of combination bands due to stretching and bending carbon–hydrogen

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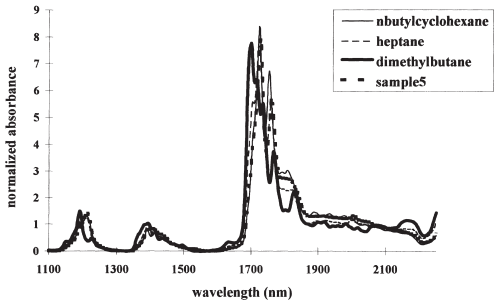

Figure 1. Near-infrared spectra of n-heptane, 2,3-dimethylbutane, n-butylcyclohexane and sample 5.

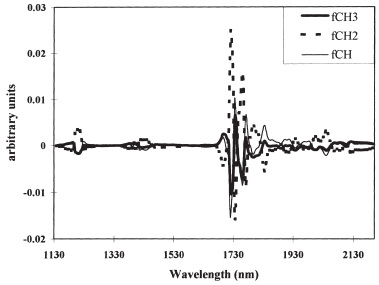

Figure 2. Plot of the product of the PLS model regression coefficients (four latent variables) for f_{CH3}, f_{CH2} and f_{CH} by an average *X* vector vs the wavelengths.

bond vibrations. The first overtone of the fundamental stretching vibrations of the carbon-hydrogen bond lies from 1680 to 1800 nm (CH_3: 1695–1705 nm, CH_2: 1725–1765 nm) (see Figure 1).

A set of *X*-variables was prepared by cutting out the noisy parts at the extremities of the NIR spectrum and the areas around the baseline correction points. This set, constituted by 433 absorbance values, was mean-centered and scaled. The computed PLS model has minimum values of the *SDEP*, for the three *Y* variables, corresponding to four latent variables (*LV*s). These values, computed either by LOO or by grouped cross-validation (see Table 1), are very similar, thus indicating a fairly stable model.

The products of the regression coefficients of the model for the different CH_* groups by an average **X** vector are plotted against the wavelengths in Figure 2. The figure shows the most important variables in the spectrum, corresponding to the specific absortion bands of the respective CH_* groups. The f_{CH3}, f_{CH2} and f_{CH} predicted values for the calibration samples, obtained with the LOO cross-validation method, are reported in Table 2 and plotted v. the actual values in Figure 3 to point out the predictive capability of the model. The correlation coefficients (R^2) for f_{CH3}, f_{CH2} and f_{CH} are respectively 0.992, 0.990 and 0.967.

The variable Q has been defined as the ratio $(n_{CH3} + n_{CH}) / n_{CH2}$, equivalent to the ratio $(f_{CH3}+f_{CH})/f_{CH2}$ and calculated for the total paraffins from the hydroisomerisation process. Actually, an increase in isoparaffin content produces an increase of the average number of CH_3 and CH groups and a correlation is expected between Q and the average branching degree or the average number of ramifications in the sample which depends of the concentration of the isoparaffins formed during the pro-

Table 1. *SDEP* values corresponding to different cross-validations of the PLS for the prediction of molar fractions of the CH_3, CH_2 and CH groups in paraffins model (four latent variables).

Cross-validation method	19 segments (LOO)	9 segments	6 segments	4 segments
SDEP (f_{CH3})	0.0171	0.0182	0.0194	0.0197
SDEP (f_{CH2})	0.0288	0.0274	0.0298	0.0279
SDEP (f_{CH})	0.0196	0.0169	0.0183	0.0181

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Table 2. Model compounds (calibration set). Actual and calculated molar fractions of the CH_3, CH_2 and CH groups (four latent variables).

Model compounds	f_{CH3} actual	f_{CH3} predict.	error	f_{CH2} actual	f_{CH2} predict.	error	f_{CH} actual	f_{CH} predict.	error
pentane	0.400	0.405	0.005	0.600	0.582	–0.018	0.000	0.014	0.014
hexane	0.333	0.337	0.004	0.667	0.667	0.000	0.000	–0.003	–0.003
heptane	0.286	0.301	0.015	0.714	0.700	–0.014	0.000	–0.001	–0.001
octane	0.250	0.266	0.016	0.750	0.735	–0.015	0.000	–0.001	–0.001
nonane	0.222	0.238	0.016	0.778	0.766	–0.012	0.000	–0.004	–0.004
decane	0.200	0.220	0.020	0.800	0.776	–0.024	0.000	0.004	0.004
tetradecane	0.143	0.135	–0.008	0.857	0.882	0.025	0.000	–0.018	–0.018
hexadecane	0.125	0.101	–0.024	0.875	0.919	0.044	0.000	–0.021	–0.021
octacosane	0.071	0.077	0.005	0.929	0.914	-0.015	0.000	0.010	0.010
dotriacontane	0.063	0.057	–0.005	0.938	0.906	-0.032	0.000	0.037	0.037
squalane	0.267	0.262	–0.005	0.533	0.549	0.016	0.200	0.189	–0.011
tetramethyl-pentadecane	0.316	0.309	–0.007	0.474	0.477	0.003	0.211	0.214	0.003
iso-octane	0.714	0.670	–0.044	0.143	0.186	0.043	0.143	0.145	0.002
2,3-dimethyl-butane	0.667	0.689	0.022	0.000	0.011	0.011	0.333	0.300	–0.033
2-methyl-butane	0.600	0.561	–0.039	0.200	0.243	0.043	0.200	0.196	–0.004
cyclohexane	0.000	-0.006	–0.006	1.000	1.005	0.005	0.000	0.001	0.001
decahydro-naphtalene	0.000	-0.002	–0.002	0.800	0.836	0.036	0.200	0.166	–0.034
n-butyl-cyclohexane	0.100	0.092	–0.008	0.800	0.810	0.010	0.100	0.097	–0.003
t-butyl-cyclohexane	0.333	0.353	0.020	0.556	0.491	-0.065	0.111	0.157	0.046

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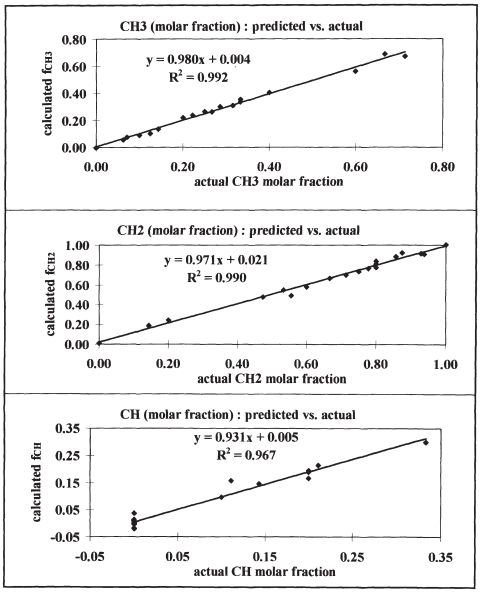

Figure 3. Model compounds (calibration set). Molar fractions of the CH_3, CH_2 and CH groups: predicted vs actual values.

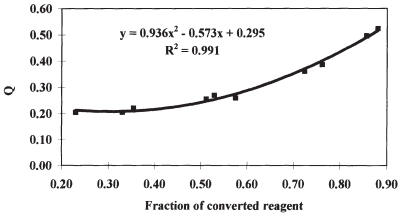

Figure 4. Plot of the ratio *Q* calculated for the samples from the hydromerisation process versus the fraction of converted reagent (linear hexadecane).

cess. The molar fractions f_{CH3}, f_{CH2} and f_{CH} of the samples from the hydroisomerisation process have been estimated applying the PLS model to their NIR spectra and used to calculate Q. The results are presented in Table 3. A plot of Q against the fraction of converted reagent is shown in Figure 4. A good correlation ($R^2 = 0.99$) is obtained with a quadratic fit corresponding to the equation:

$$[Q] = 0.936\,x^2 - 0.573\,x + 0.295$$

where x is the fraction of converted hexadecane.

The main deviation from linearity is observed at higher conversions. An explanation could be that a gradual overcome of the catalytic hydroisomerisation by cracking reactions causes a strong increase

Table 3. Samples from the hydroisomerization unit. Fraction of converted reagent (n-C_{16}) and predicted values of the molar fractions of the CH_3, CH_2 and CH groups.

	converted n-C_{16}	f_{CH3}	f_{CH2}	f_{CH}	$Q = f_{CH3}+f_{CH}/f_{CH2}$
Sample 1	0.230	0.120	0.830	0.050	0.205
Sample 2	0.330	0.126	0.830	0.044	0.205
Sample 3	0.354	0.130	0.819	0.051	0.221
Sample 4	0.511	0.145	0.797	0.059	0.255
Sample 5	0.529	0.147	0.787	0.066	0.271
Sample 6	0.575	0.146	0.793	0.060	0.260
Sample 7	0.724	0.182	0.735	0.084	0.362
Sample 8	0.761	0.187	0.721	0.092	0.387
Sample 9	0.856	0.225	0.668	0.107	0.497
Sample 10	0.880	0.234	0.656	0.110	0.524

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of terminal CH_3 groups. Actually, the increase of products from cracking as the fraction of converted n-paraffin increases has been demonstrated.[12]

Although further work with NIR is needed to have a better characterisation of the ratio isomers/cracking products during the process and to extend the model to other linear paraffinic feedstocks, these first results are promising for what concerns the feasibility of NIR/PLS to monitor the hydroisomerisation process.

Conclusions

Although the absorption and combination bands of the various types of hydrocarbon C–H bonds are broad overlapping features in the near infrared region of the spectrum, a multivariate statistical method such as PLS can be applied to near infrared spectra to estimate the ratio $Q = (n_{CH3} + n_{CH})/n_{CH2}$ correlated to n-paraffin conversion in hydroisomerisation process. The advantage of the NIR/PLS approach is its speed and simplicity compared to more traditional methods. Moreover, the use of fibre optics allows it to be used on-line.

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