USING NMR TO PREDICT THE PRODUCTION OF LIGHT OLEFINS

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Aiming to supply the demand of the Brazilian petrochemical industry, Petrobras has been studying ways to maximize the production of light olefins, mainly ethene and propene. The chemical characterization of available feedstock is essential for the production of those olefins and critical for an economical solution providing also the possibility of selection of adequate streams. In this work we have developed a model for predicting the production of light olefins using the strategy shown in figure 1 bellow.

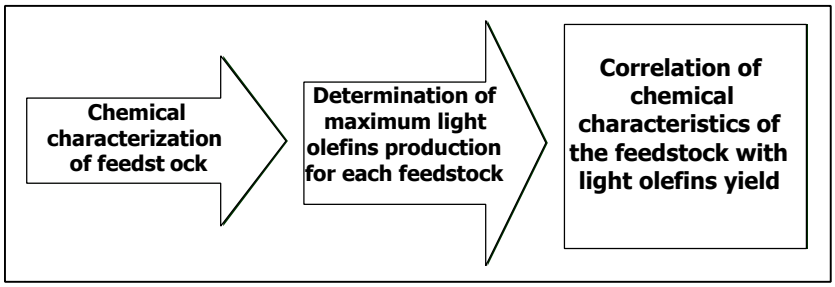

Figure 1 – Strategy used for prediction of the production of light olefins

Fourteen petroleum streams were selected and evaluated for the production of light olefins in a fluidized bed bench scale unit with at a constant reaction temperature (600ºC). Due to the diversity of the selected streams, the amount of ZSM-5 zeolite in the catalyst was optimized in order to maximize the production of light olefins. The total amount of ethene and propene (LO) was determined for each stream using a catalyst/oil ratio of 8,0.

The streams were characterized by ^{1}H and ^{13}C NMR spectroscopy. The NMR spectra were obtained in a Varian Inova-300 equipment (7.05T of magnetic field) using quantitative experimental conditions, room temperature and a 5mm probe. The ^{1}H spectra of 5%v/v solutions in 1:1 de $CDCl_3$:C_2Cl_4, were acquired at 300 MHz using 45°rf pulses, 1.0 s of pulse delay and 128 transients were accumulated. The ^{13}C spectra of 40% v/v solutions of samples in $CDCl_3$ containing 0.05mL^{-1} of cromium acetylacetonate (relaxation reagent) were obtained at 75.4MHz using 90° rf pulses, 10s of pulse delay, and the decoupler in the gated mode to avoid NOE. The spectra were referenced by the $CDCl_3$ peak at 7.24ppm (^{1}H) and 77ppm (central) (^{13}C) respectively. Each spectrum was integrated in certain regions and the average molecular parameters were calculated for each sample[1] (Table 1).

From NMR data and the LO results, a statistic study using the Statistica program was carried out in order to identify which experimental parameters are able to respond and to influence in the performance of the production of light olefins. The statistic analysis of the 14 streams, using the “Forward Stepwise” technique, identified two significant variables from NMR data: TAMALQ (average molecular chain lenght of linear alkanes) and HOL (molar % of olefinic hydrogens). These two variables generated an equation to calculate the total amount of light olefins from NMR data (PILO). The regression analysis is illustrated in figure 2 and has shown a correlation coefficient R^2 of 0.891.

Table 1 – Some molecular parameters obtained from NMR spectra

Average Molecular Parameter	Chemical shift (ppm)
^{13}C NMR SPECTRA	
Aromatic carbons **(CARO)**	160 - 100
Aliphatic carbons **(CSAT)**	70 - 0
γ carbons in a paraffinic straight chain **($C\gamma$)**	32,2
β carbons **(C_β)**	22,9
δ or further removed carbons in a paraffinic straight chain **(C_δ)**	29,7
α carbons in a paraffinic straight chain **(C_α)**	14,1
^{1}H NMR SPECTRA	
Aromatic Hydrogens **(HARO)**	9 - 6
Olefinic Hydrogens **(HOL)**	6 – 4.5
Aliphatic Hydrogens **(HSAT)**	0 – 4.5
CALCULATED PARAMETERS	
Average molecular chain lenght **(TMALQ)**	[2x(Cα + Cβ + Cγ + Cδ) / Cα]

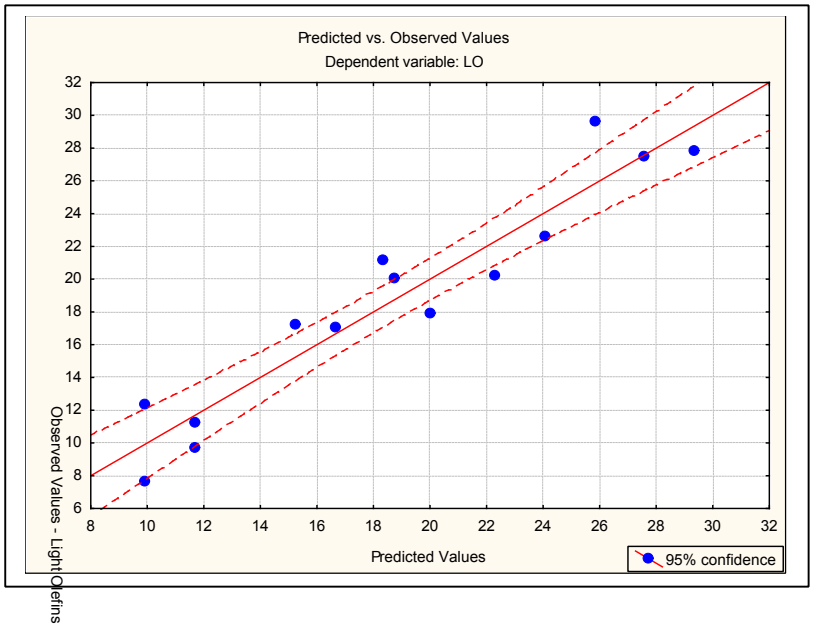

Figure 2 – Correlation curve: Observed values (LO) x predicted values from NMR (PILO)

The study has shown that only two parameters obtained from NMR data are enough to generate an efficient model to predict the potential of a feedstock to generate light olefins. This will be of most importance for the selection of available refinery streams considering also economical factors, in order to supply the demand of the Brazilian petrochemical industry.

REFERENCES

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