Application of H-NMR for FCC Feed Characterization

Dariusz S. Orlicki[1], Uriel Navarro[1], Michelle Ni and Larry Langan

Dariusz.Orlicki@Grace.com; Uriel.Navarro@Grace.com; Weijuan.M.Ni@Grace.com
Larry.Langan@Grace.com

Grace Davison[2] Refining Technologies

ABSTRACT

In this paper we discuss application of ^{1}H-NMR for FCC feed characterization. A set of forty two FCC feeds from the Grace Davison Feed Database, representing a range of ^{o}APIs from 13.9 to 32.4, was fully characterized by measuring bulk physical properties, distillation curve, Conradson carbon residue, refractive index, and metal content (V, Ni, Fe, Na, and others). All these feeds were also characterized by ^{1}H-NMR, SARA, and UV-VIS techniques. In addition, ACE testing was conducted on all of these feeds using two typical FCC catalysts. Using statistical tests, applicability of ^{1}H-NMR feed characterization to predict feed bulk physical properties and ACE yields was examined. Results were compared against correlations published in literature.

Keywords: ^{1}H-NMR, feed characterization, ACE testing

1. INTRODUCTION

Feed is considered the most influential single factor affecting the FCC unit performance. Chemical composition of the FCC feed affects yields and quality of products. The FCC feed properties strongly depend on two factors: the geographic source of the crude and initial preprocessing. To make things even more complicated, FCC feeds are usually blends of multiple feed sources and refinery recycle streams, some of them very poor quality. Therefore knowing molecular composition and concentrations of a complex feed is essential not only for optimal FCC unit operations but also in a process of catalyst selection and products yield predictions. In general, the currently used typical analytical techniques for feed characterization provide helpful information about feed quality but they are not adequate to provide the identities and concentrations of the molecules in commercial FCC feeds. Over the years, methods have been developed, mostly in the form of heuristic correlations, to predict important FCC feed properties such as hydrogen content, type of carbon (aromatic - Ca, paraffinic – Cp, and naphthenic - Cn), molecular weight, etc., with a goal to relate these feed quality characteristics to product yield and qualities. However, there are certain limitations in employing these techniques that

[1] Author of correspondence
[2] Grace Davison is a business unit of W.R. Grace & Co.-Conn.

include the range for which these correlations were developed and assumptions and mathematical manipulation involved in the derivation of such formulas.
^{1}H-NMR technique alone or in combination with ^{13}C-NMR has been already successfully employed in numerous scientific studies to characterize complex FCC feeds [1]. Although this technique provides unparallel level of information about atomic connectivity, it may be less precise in predicting molecular composition of the feed. There are reports published in literature about applications of ^{1}H-NMR to predict properties of FCC feeds [2] or FCC products [3, 4]. Although these papers proclaimed great potential in using NMR techniques for characterization and prediction of feed properties, one has to be cautioned when applying these findings. The analyses were performed on either feeds originated from the same geographical region (Colombian crudes) or products of the same nature (gasoline) that imposes some limitations on potential application of these findings.

In this work, a set of forty two FCC feeds representing diverse geographical locations ranging from Asia Pacific through Europe to different regions within continental United States and Canada was selected from the Grace Davison Feed Database. The selection criterion was based solely on ^{o}API that was selected to cover the widest possible range. In this study the range of ^{o}API was between 13.8 and 32.3. All feeds were fully characterized by measuring bulk physical properties, distillation curve, Conradson carbon residue, refractive index, and metal content (V, Ni, Fe, Na, and others). Table 1 lists some of the properties measured along with the average and minimum and maximum values for the set of feeds. Consequently, feeds were characterized by ^{1}H-NMR and chemical shift spectra over the range of 0.5 to 9.3 ppm were collected. This information was used to find statistical correlations between feed spectra and properties.

Advance **C**atalyst **E**valuation unit ACE [5] was used to study catalyst-feed interactions. The reactor temperature was set at 980 ^{o}F (799.8 K). Every feed was tested on a commercially available FCC catalyst, supplied by Grace Davison, at three different cat-to-oil ratios, 4, 6, and 8. The feed was injected at a constant rate of 3 g/min for 30 seconds. The catalyst to oil ratio was adjusted by varying the amount of catalyst in the reactor. Two catalysts used for this evaluation were laboratory deactivated using **C**yclic **P**ropylene **S**teaming (CPS) method [6]. Properties of these catalysts after deactivation are listed in Table 2.

2. EXPERIMENTAL

The ^{1}H NMR spectra of FCC feed were recorded on a Bruker DRX 400 MHz NMR spectrometer. The concentration of the samples as ~5 wt % in $CDCl_3$ was recommended by Molina, Navarro and Murgich [2] to avoid concentration dependence of the chemical shift. The 30^{o} pulse sequence was applied, with 4.089 s acquisition time, 2 s pulse delay [2], 8012.8 Hz spectral width and 64 scans. Hexamethyldisiloxane (HMDSO) was used as reference. NMR processing was realized using MestReNova software. The phase and baseline of the resulting spectra was manually adjusted and corrected. The spectra were integrated six times and average values were taken for the purpose of calculations. The

spectrum was divided into 12 regions, representing 12 different hydrogen types [2] in feed (see table 3). Figure 1 shows a sample of feed ^{1}HNMR spectrum. The average integrals of each segment were correlated with the physicochemical properties.

Table 1. Properties of the 42-feed sample

Property	Minimum	Maximum	Average
^{o}API	**13.8**	**32.3**	**22.0**
Average **M**olecular **W**eight	**264**	**624**	**375**
Ca	**0**	**43.6**	**23.8**
Cn	**0**	**37.1**	**18.5**
Cp	**0**	**67.4**	**55.3**
Basic Nitrogen	**0**	**0.20**	**0.05**
Total Nitrogen	**0.009**	**0.36**	**0.12**
Sulfur	**0.01**	**3.994**	**1.264**
Nickel [ppm]	**0**	**6.9**	**1.21**
Vanadium [ppm]	**0**	**16.5**	**2.0**
Hydrogen Content	**10.4**	**13.7**	**12.0**
Conradson carbon	**0**	**9.8**	**1.28**
K Factor	**10.8**	**12.3**	**11.6**
Refractive Index	**1.477**	**1.557**	**1.517**
Initial **B**oiling **P**oint (**IBP**) [^{o}F]	**287**	**709**	**376**
5% [^{o}F]	**375**	**881**	**529**
10% [^{o}F]	**458**	**940**	**603**
20% [^{o}F]	**542**	**1015**	**674**
30% [^{o}F]	**576**	**1064**	**718**
40% [^{o}F]	**611**	**1103**	**756**
50% [^{o}F]	**643**	**1143**	**792**
60% [^{o}F]	**675**	**1185**	**829**
70% [^{o}F]	**710**	**1238**	**871**
80% [^{o}F]	**747**	**1311**	**922**
90% [^{o}F]	**810**	**1383**	**1002**
95% [^{o}F]	**876**	**1383**	**1063**
Final **B**oiling **P**oint (**FBP**) [^{o}F]	**1007**	**1383**	**1183**

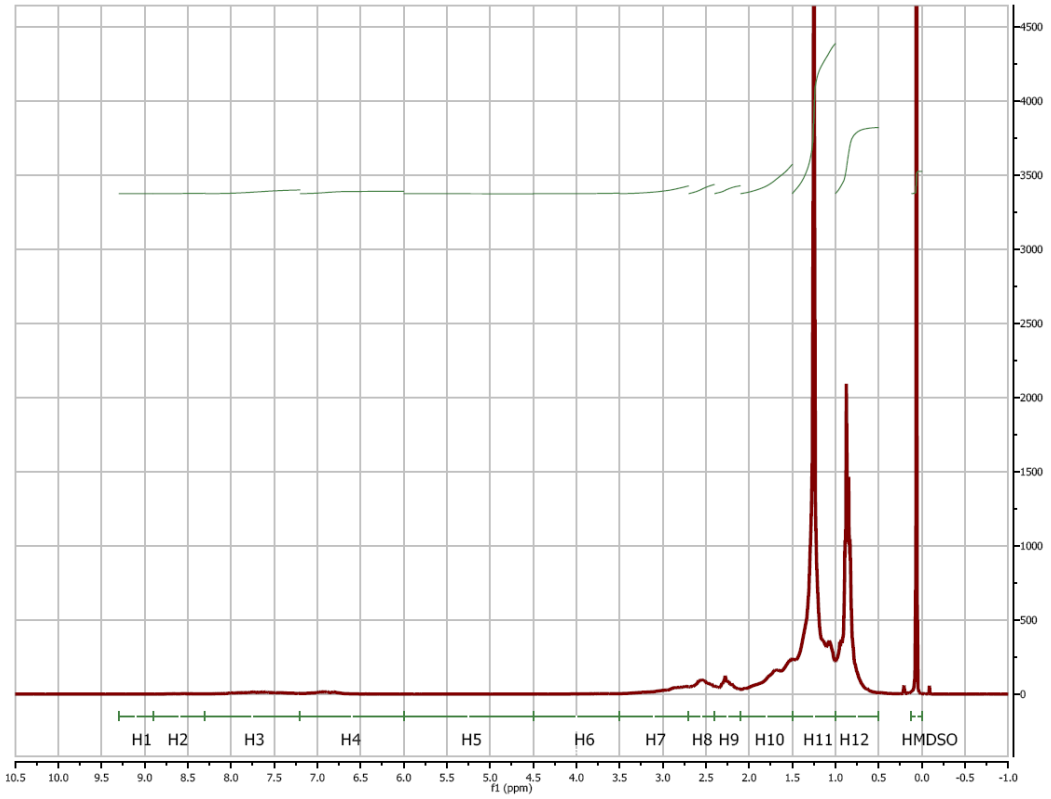
Table 2. Properties of two commercial catalysts deactivated in the laboratory by CPS method.

Catalyst	Total Surface Area [m^2/g]	Zeolite Surface Area [m^2/g]	Matrix Surface Area [m^2/g]	Unit Cell Size [Å]
Catalyst A 5% (Re_2O_3)	**187**	**149**	**38**	**24.28**
Catalyst B 2% (Re_2O_3)	**175**	**92**	**83**	**24.29**

Table 3. 1H NMR regions and their corresponding hydrogen types

Chemical shift region (ppm)	Area	Hydrogen Type
0.5-1.0	H1	CH_3 and some naphthenic CH and CH_2
1.0-1.7	H2	CH_2 and some □CH
1.7-1.9	H3	CH and CH_2 in □□positions
1.9-2.1	H4	CH_3s in olefins
2.1-2.4	H5	CH_3s in aromatic carbons
2.4-3.5	H6	CH and □CH_2 in aromatic carbons
3.5-4.5	H7	bridging CH_2
4.5-6.0	H8	olefins
6.0-7.2	H9	mono-aromatics
7.2-8.3	H10	di-aromatics and some tetra-aromatics
8.3-8.9	H11	tri- and tetra-aromatics
8.9-9.3	H12	some tetra- aromatics

Figure 1. ^{1}H-NMR spectrum of one feed. The assigned regions (H1 to H12) are listed in Table 3.



3. RESULTS AND DISCUSSION

3.1 Physicochemical properties

The physicochemical properties of the feeds were determined by appropriate ASTM methods. One of the objectives of this study was to evaluate possibility to use ^{1}H-NMR spectra to predict these properties.

3.1.1 API Gravity

The American Petroleum Institute API gravity is a measure of feed density compared to water. The formula used to obtain the API gravity of petroleum liquids is as follows:

$$\text{API gravity} = \frac{141.5}{SpGr\ (60\ ^{\circ}\text{F})} - 131.5$$

Specific gravity of petroleum products is measured at 60 ^{o}F. The values of Specific Gravity vary over a relatively narrow range from about 0.8 for very light paraffinic crudes to about 1.0 for heavy highly asphaltic crudes. The API formula maps that narrow band of Specific Gravity values onto a stretched range with values between 10 and 40. The API is one of the most important properties of petroleum products because it can be easily and precisely measured and it is a good indicator of the feed quality. It correlates well with many feed properties such as:

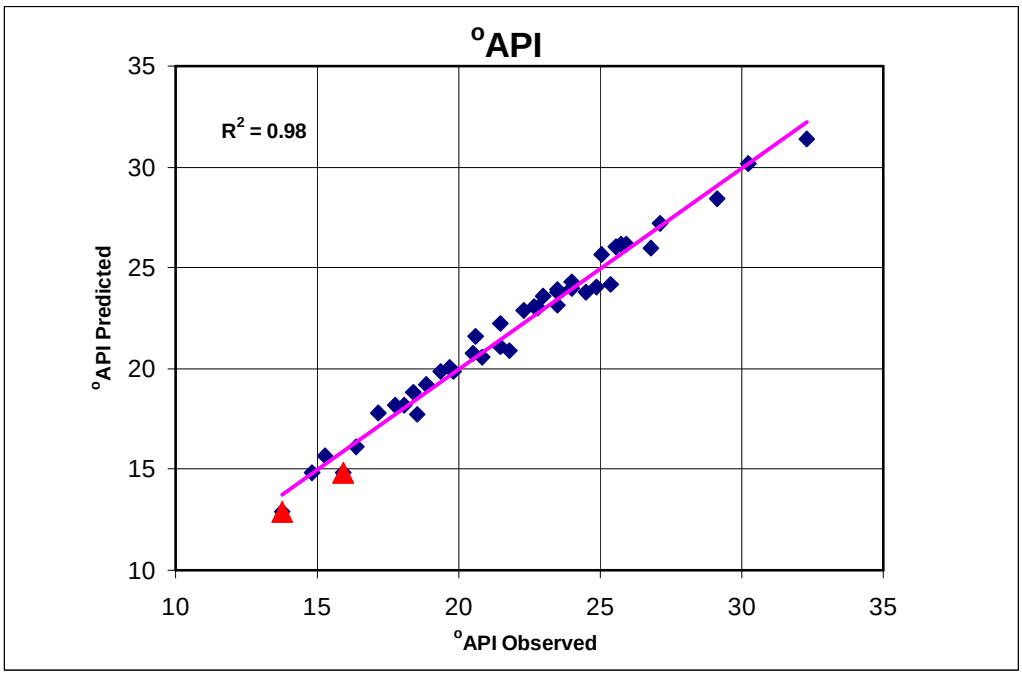
- $\%C_A$, $\%C_N$, and $\%C_P$ representing the distribution of carbon atoms between the three structures, aromatic, naphthenic, and paraffinic [7],
- Refractive Index that is proportional to feed's aromatic content [8],
- UOP K-factor, a composite parameter that estimates either paraffinicity or naphthenicity [9],
- Molecular weight [7] and structure of hydrocarbons through the concept of molar volume [10].

SAS Enterprise Guide was used to analyze data. The best linear regression model to predict ^{o}API based on ^{1}H-NMR spectra has the form:

$$\text{API} = 31.170 + 2.932 * \text{H5} - 3.934 * \text{H7} + 1.779 * \text{H9} - 1.191 * \text{H10} + 0.458 * \text{H12}$$

The coefficient of determination R^2 for the API model is 0.98. Figure 2 shows ^{o}API observed versus model calculated. The two points with the highest error of 6.7% and 6.5% are marked as green triangles.

Figure 2 °API predicted based on ^{1}H-NMR versus observed



3.1.2 UOP K factor

The UOP K factor is indicative of feed nature. Values of 12.0 or higher indicate a product of paraffinic nature; naphthenic feeds have values between 11.6-11.9; while aromatic feeds have values less than 11.5. This composite factor can be calculated according to the equation:

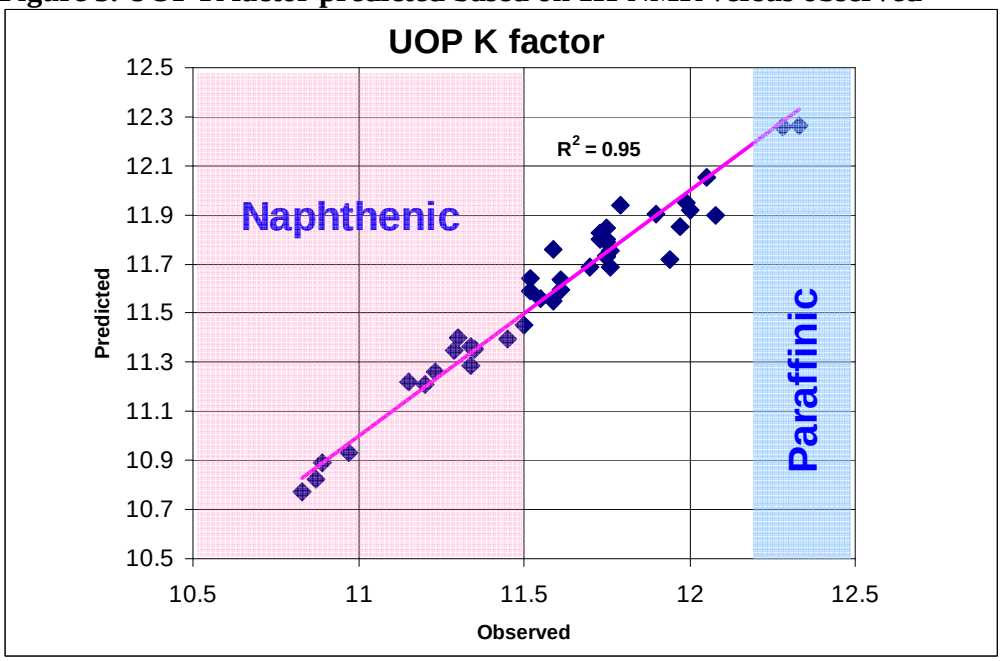
$$K = \sqrt[3]{\frac{(MeABP + 460)}{SpGr}}$$

where MeABP stands for atmospheric equivalent boiling point and SpGr is specific gravity at 60 °F. The best linear regression model to predict UOP K factor based on ^{1}H-NMR spectra has the form:

$$K = 13.183 - 0.203 * H3 + 0.128 * H4 + 0.198 * H7 - 0.295 * H9 - 0.09 * H10$$

The coefficient of determination R^2 for UOP K factor model prediction is 0.95 and the maximum error is less than 1.9%. It may be interesting to notice that the ^{1}H-NMR predicted values follow more closely the calculated UOP K factor in the paraffinic and naphthenic regions. The average error in the intermediate region where $11.5 < K < 12.2$ is 0.6% compared to 0.4% in the other two regions. The coefficient of determination R^2 for the intermediate region is 0.83 while for the paraffinic and naphthenic regions is over 0.99. Figure 3 shows UOP K observed versus estimated from ^{1}H-NMR spectra.

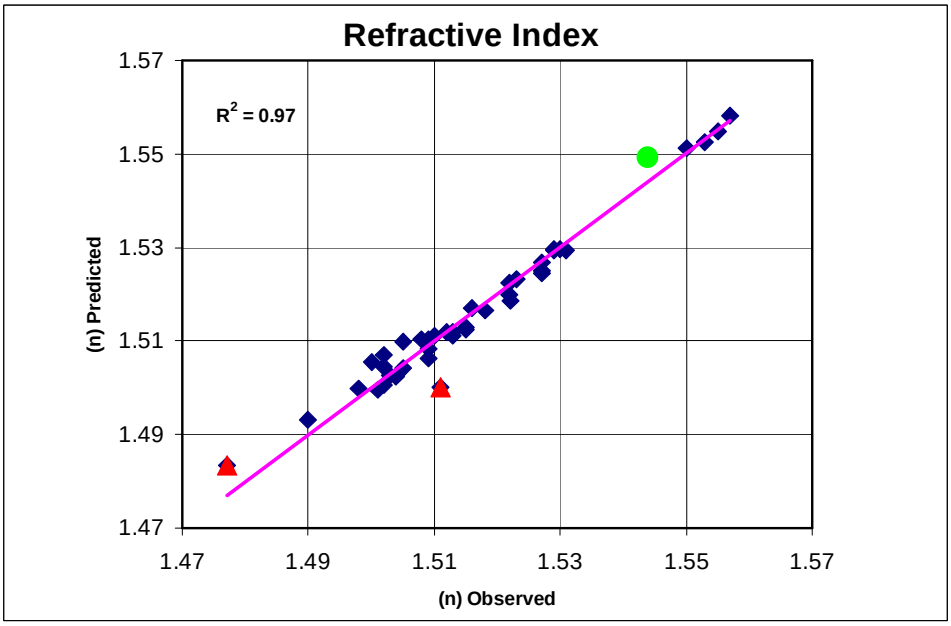
Figure 3. UOP K factor predicted based on 1H-NMR versus observed



3.1.3 Refractive index (n)

Refractive index (n) of a feed sample is proportional to its aromatic content, the higher the value the more aromatic compounds are in the feed.

Figure 4. Refractive index (n) predicted based on ^{1}H-NMR versus observed.



There are many methods to predict composition of petroleum products based on refractive index measurements [11]. The best linear regression model to predict (n) refractive index based on ^{1}H-NMR spectra has the form:

$$n = 1.2614 + 0.0046 * H3 - 0.0091 * H5 + 0.0173 * H7 + 0.005 * H10 + 0.0027 * H11$$

The coefficient of determination R^2 for model prediction is 0.97 and the maximum error is less than 0.7%. Figure 4 shows refractive index (n) observed versus estimated from ^{1}H-NMR spectra. The model shows the largest discrepancies for either low aromatic content feeds - red triangles, or high aromatic content feeds – green circle.

3.1.4 Distribution of aromatic carbon (Ca), naphthenic carbon (Cn), and paraffinic carbon (Cp)

Information about feed composition can be inferred from other measured properties of the feed such as refractive index (n), density (d), and molecular weight (M). In the n-d-M method [13], the distribution of carbon atoms among aromatic, naphthenic, and paraffinic groups of the petroleum product is calculated using empirical formulas. The Ca, Cn, and Cp represent the percent of carbon atoms in aromatic, naphthenic, and paraffinic structures respectively. In theory, ^{1}H-NMR should be able to distinguish hydrogen distribution between aromatic and aliphatic structures thus yielding information on feed composition. The best linear regression model to predict Ca based on the ^{1}H-NMR spectra has the form:

$$Ca = 24.8728 - 10.8938 * H1 + 6.0229 * H2 - 2.5847 * H4 + 4.5356 * H7 - 0.455 * H12$$

Figure 5. Ca predicted based on ^{1}H-NMR spectra versus observed

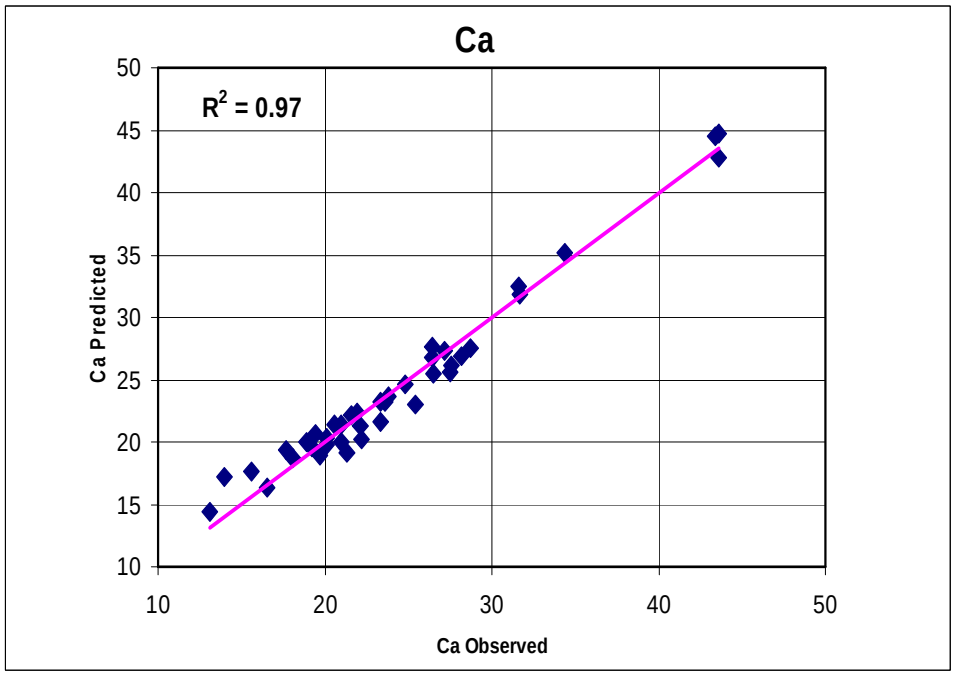


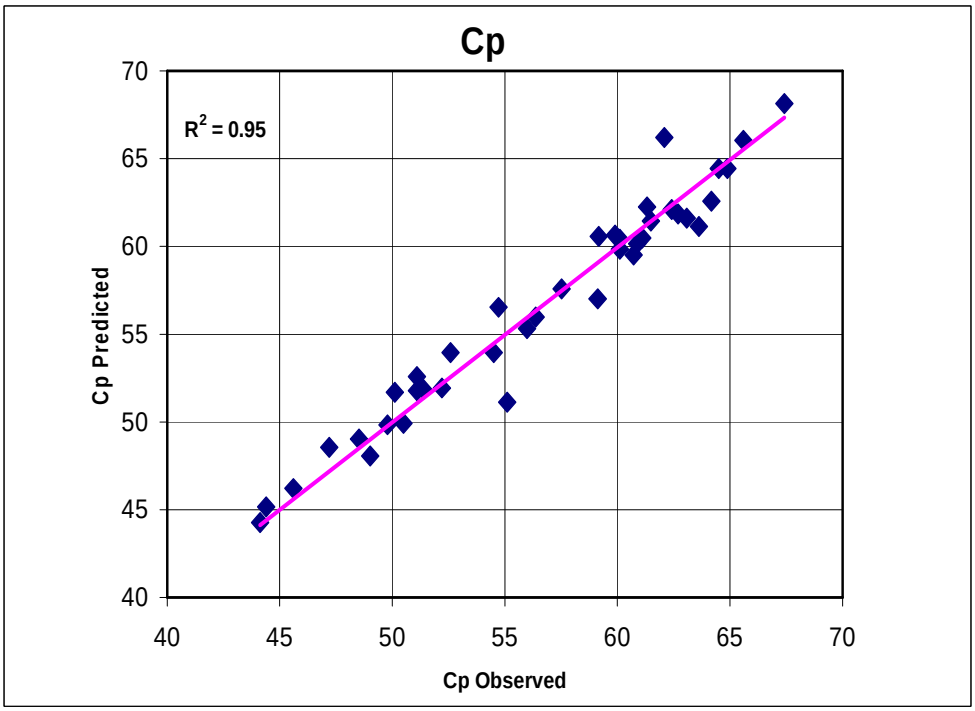
Figure 5 shows percent of aromatic carbon content estimated from ^{1}H-NMR spectra versus observed (n-d-M method). The coefficient of determination R^2 for Ca model prediction is 0.97. Although the maximum error for Ca prediction is less than 3.5%, the relative error for low values of Ca can be as high as 23%.

The best linear regression model to predict Cp based on the ^{1}H-NMR spectra has the form:

$$Cp = -11.8104 + 11.6713 * H1 - 11.1448 * H2 + 4.9076 * H6 + 1.3808 * H8 + 1.2682 * H11$$

The coefficient of determination R^2 of the Cp model is 0.95. The maximum error for Cp prediction can be as high as 7%. Figure 6 shows percent of paraffinic carbon content Cp estimated from ^{1}H-NMR spectra versus observed (n-d-M method). The percent of naphthenic carbon Cn can be found directly by regression method or more accurately by difference:

Figure 6. Cp predicted based on ^{1}H-NMR spectra versus observed.



The naphthenic carbon (Cn) can be calculated for the following equation:

$$Cn = 100 - Ca - Cp$$

The coefficient of determination R^2 for Cn model prediction is 0.88 and the maximum error is below 8%.

3.1.5 Correlation index CI

Correlation index CI was originally devised by H.M. Smith from the US Bureau of Mines in 1940 and it relates the average boiling point of a feed to its specific gravity. It is defined by the following empirical formula:

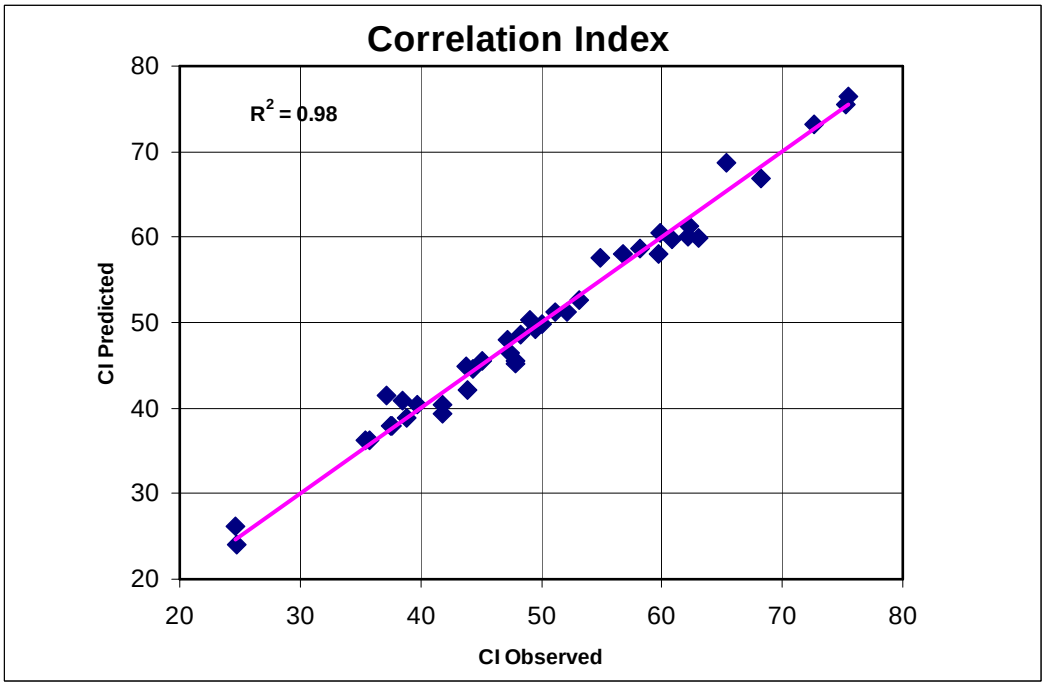
$$CI = \frac{87552}{(MeABP + 460)} + \frac{67030}{(^{o}API + 131.5)} - 456.8$$

where MeABP (in Fahrenheit) is average boiling point defined as the arithmetic average of the temperatures taken at 10% intervals from 10% to 90%. The index can be used to classify feeds: values below 42 indicate paraffinic feeds, values between 42-55 correspond to naphthenic feeds, while those higher than 55 are aromatic. The best linear regression model to predict correlation index CI has the form:

$$CI = -45.3116 + 5.3186 * H3 + 2.37 * H7 + 4.478 * H10 + 0.4727 * H11$$

The coefficient of determination R^2 of the CI model is 0.98. The maximum error for CI prediction is below 7%. Figure 7 shows CI estimated from ^{1}H-NMR spectra versus calculated from original formula.

Figure 7. Correlation index CI predicted from 1H-NMR spectra versus calculated from original H.M. Smith's formula.



3.1.6 Hydrogen Content

The hydrogen content of the FCC feeds is one of the most important physicochemical properties to define the feed quality. The amount of hydrogen is related with hydrocarbon types and with the crackeability of the feed. The following equation predicts the feed hydrogen content:

Hydrogen = 20.692-0.2673*H10-0.06788*H11- 0.336479*H3 + 0.8453*H6-0.44595*H7

3.2 Catalyst feed interactions - ACE yield predictions

ACE fluidized bed microactivity unit was used to study the catalyst and feed interactions. Fluidized bed reactor was operated at 980 ^{o}F (799.8 K). Every feed was tested on two different catalysts at three cat-to-oil ratios 4, 6, and 8. Properties of laboratory deactivated catalysts A and B are shown in Table 2. The feed temperature was kept at 170 ^{o}F (349.8 K). The injection rate was 3 g/min and the injection time was 30 s. Products of the cracking reactions were analyzed by GC, PONA, and SYMDIS.

3.2.1 Conversion

By definition, conversion is calculated as: Conversion = 100 – LCO – Bottoms. The best linear regression model to predict conversion for catalyst A has the form:

$$\text{Conversion(A)} = 72.66 + 2.77 * (\text{C/O}) - 3.063 * \text{H3} + 7.303 * \text{H4} - 10.125 * \text{H9}$$

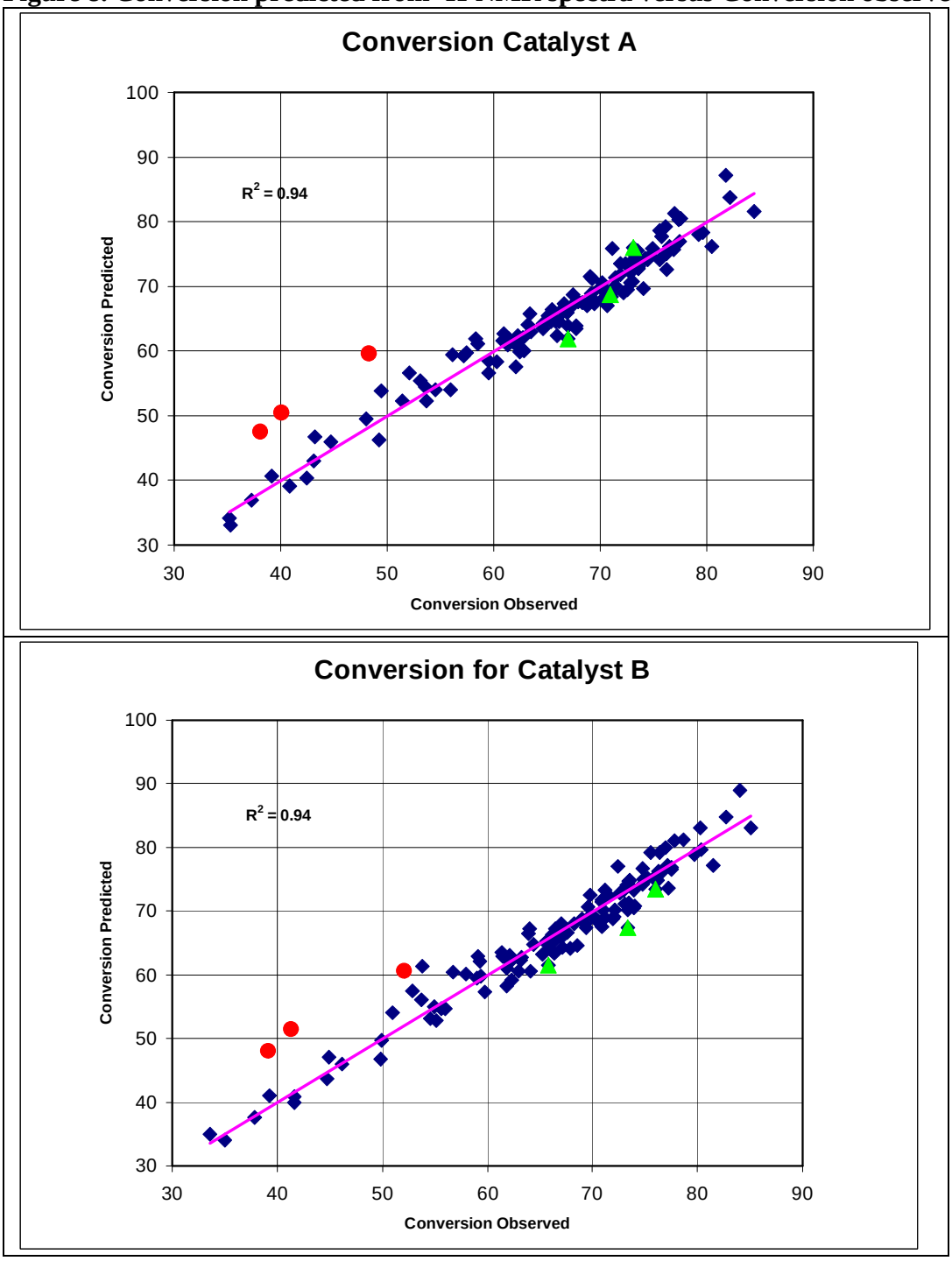
and for catalyst B

$$\text{Conversion(B)} = 72.722 + 2.998 * (\text{C/O}) - 3.016 * \text{H3} + 6.572 * \text{H4} - 9.657 * \text{H9}$$

Although the coefficients in the model for both catalysts are slightly different, the functional dependence on 1H-NMR spectra is identical. The coefficient of determination R^2 of the conversion model is 0.94 for both catalysts. Catalyst A gives higher conversion compared to catalyst B at the same cat-to-oil ratio for almost all tested feeds.

The exceptions are the heaviest feeds in the set. Figures 8 shows Conversion estimated form ^{1}H-NMR spectra Conversion observed for both catalysts A and B. The green triangles represent the heaviest feed in the study at three cat-to-oil ratios, 4, 6, and 8. The red circles correspond to three different feeds with the highest level of total nitrogen at cat-to-oil ratio 4. It looks like that nitrogen compounds interfere with catalyst activity and lower the conversion.

Figure 8. Conversion predicted from ^{1}H-NMR spectra versus Conversion observed



3.2.2 Gasoline

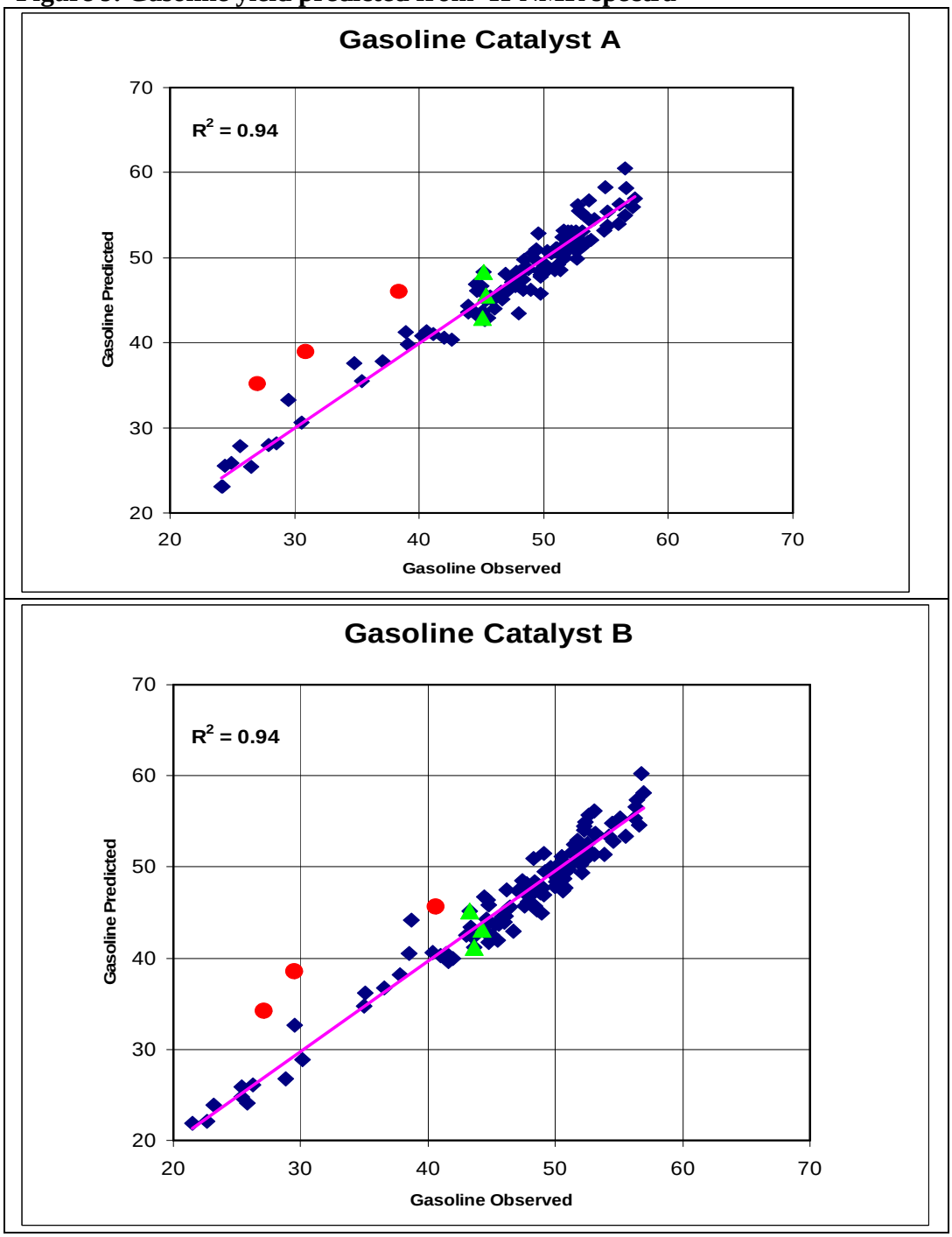
The term of gasoline includes all liquid products with a boiling point below 430 ^{o}F (494 K). The best linear regression model to predict gasoline yield has the form for catalyst A:

$$Gasoline(A) = 56.816 + 1.057 * (C/O) - 1.952 * H3 + 5.389 * H4 - 2.105 * H7 - 4.961 * H9$$

and for catalyst B

$$Gasoline(B) = 56.922 + 1.009 * (C/O) - 1.843 * H3 + 5.017 * H4 - 2.692 * H7 - 4.301 * H9$$

Figure 9. Gasoline yield predicted from ^{1}H-NMR spectra



The coefficient of determination R^2 of the gasoline model is 0.94 for both catalysts. Under comparable conditions, catalyst A always makes more gasoline than catalyst B for any feed in the study. Figures 9 shows Gasoline yield predicted from ^{1}H-NMR spectra versus Gasoline yield observed. The meaning of the green triangles and red circles is the same as it was used for conversion graphs.

3.2.3 Research Octane Number RON

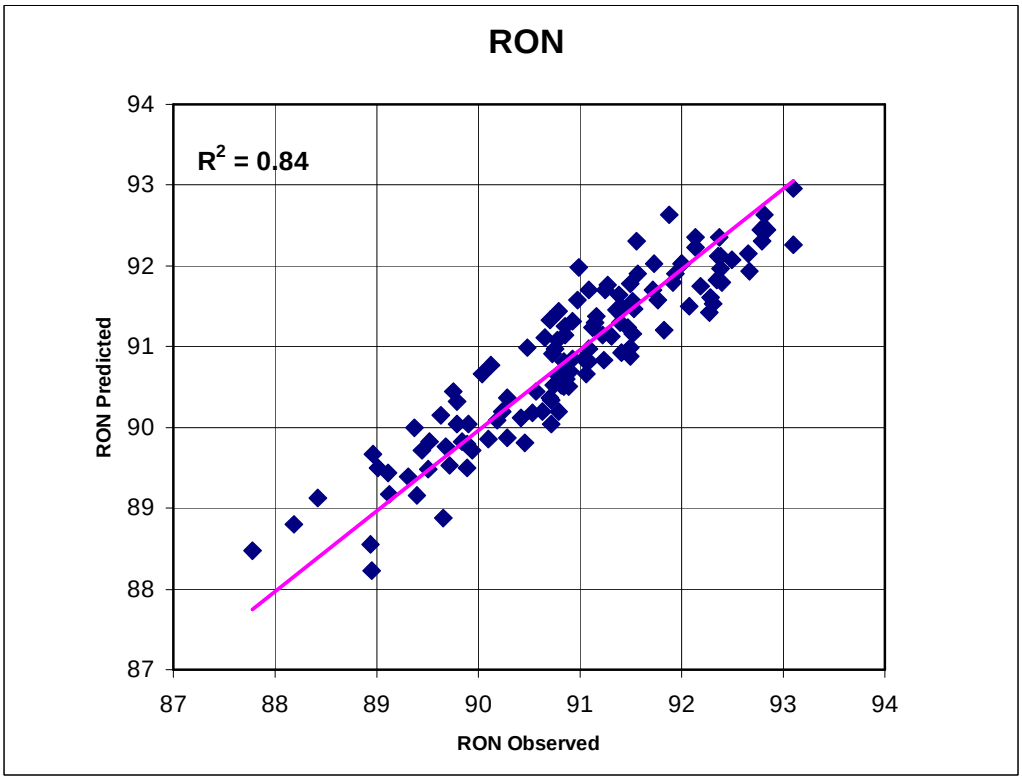
Research Octane Number is a measure of knocking characteristics of gasoline in a laboratory engine and can be used to characterize gasoline quality. The best linear regression model to predict RON for catalyst A has the form:

$$RON(A) = 85.677 + 0.168*(C/O) + 0.737*H4 - 2.359*H6 + 0.621*H7 - 0.824*H9 + 0.379*H10$$

and for catalyst B

$$RON(B) = 86.385 + 0.162*(C/O) + 0.699*H4 - 2.545*H6 + 0.672*H7 - 0.806*H9 + 0.362*H10$$

Figure 10. RON predicted from ^{1}H-NMR versus RON observed



The coefficient of determination R^2 of the RON model is 0.84 for both catalysts. Figure 10 shows RON predicted versus RON observed for catalyst B (the picture for catalyst A is quite similar). From the points uniform spread one can conclude that ^{1}H-NMR does not provide necessary information to accurately predict gasoline quality.

3.2.4 Light Cycle Oil yield (LCO)

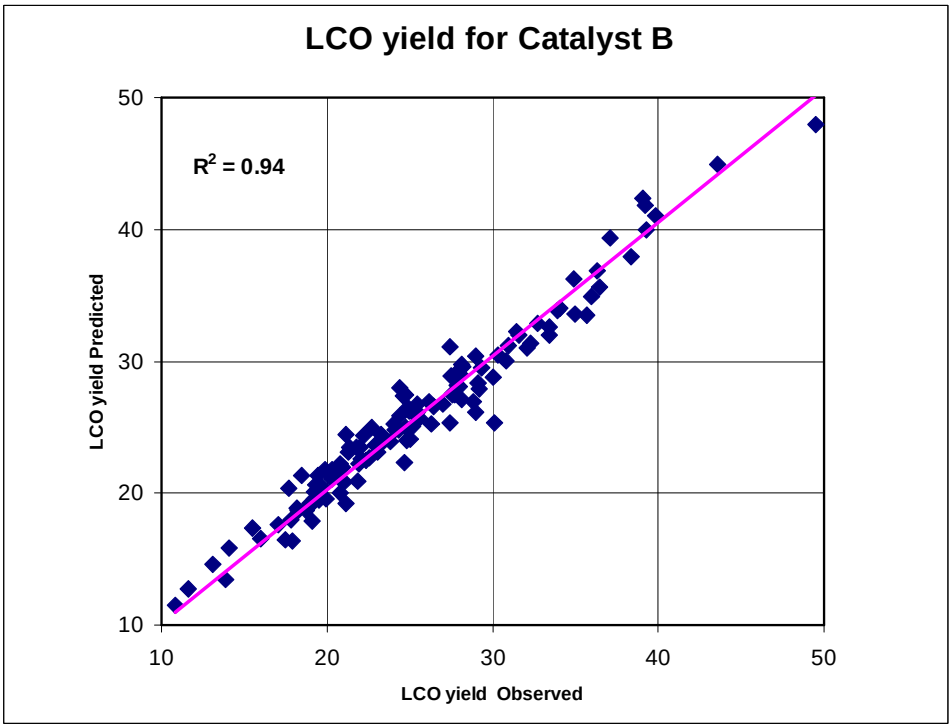
Light Cycle Oil LCO is composed of liquid products boiling in the range approximately 430 – 700 °F (494.3 – 644.3 K). The best linear regression model to predict LCO yield for catalyst A has the form:

$$LCO(A) = 76.99 - 1.486*(C/O) - 4.99*H4 + 2.389*H5 + 7.179*H9 - 1.603*H10 - 0.732*H11$$

and for catalyst B

$$LCO(B) = 80.86 - 1.53*(C/O) - 4.985*H4 + 2.563*H5 + 7.035*H9 - 1.655*H10 - 0.782*H11$$

Figure 11. LCO yield predicted from ^{1}H-NMR spectra versus LCO yield observed

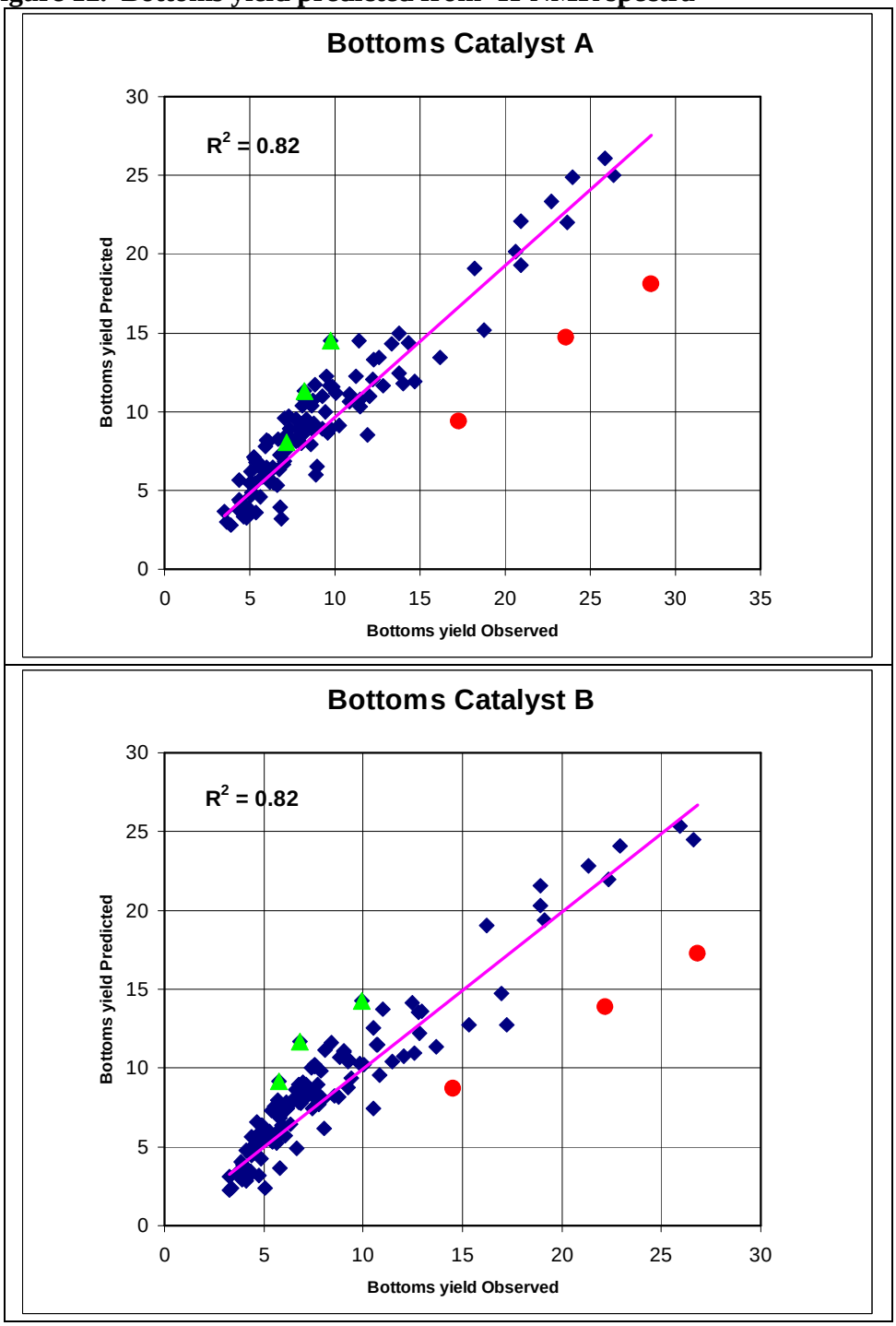


The coefficient of determination R^2 of the LCO yield model is 0.96 for catalyst A and 0.94 for catalyst B. For the same feed and under the same processing conditions catalyst B makes more LCO than catalyst A for most of the feeds tested. There are a few cases, for the heaviest feeds in the study, with no statistical difference for LCO yield between both catalysts. LCO yield predicted from 1H-NMR spectra versus LCO yield observed for catalyst B is shown in Figure 11.

3.2.5 Bottoms Yields

FCC Bottoms are defined as a blend of liquid products boiling above LCO cut point, 700° F (644.3 K). The best linear regression model to predict bottoms yield for catalyst A has the form:

Figure 12. Bottoms yield predicted from ^{1}H-NMR spectra



$$\text{Bottoms(A)} = 14.418 - 1.275 * (\text{C/O}) - 14.315 * \text{H1} + 6.836 * \text{H2} - 2.424 * \text{H4} - 1.494 * \text{H5} + 2.456 * \text{H7}$$

and for catalyst B

$$\text{Bottoms(B)} = 13.177 - 1.269 * (C/O) - 13.258 * H1 + 6.843 * H2 - 2.239 * H4 - 1.336 * H5 + 2.382 * H7$$

The coefficient of determination R^2 of the Bottoms model is 0.84 for catalyst A and 0.82 for catalyst B. Under comparable processing conditions, catalyst A always makes more Bottoms than catalyst B for any feed in the study. Figures 12 shows Bottoms yield predicted from ^{1}H-NMR spectra versus Bottoms yield observed. For heavy aromatic feeds, green triangles in the picture, the model over predicts Bottoms yield. On the other hand, the feeds with high level of nitrogen compounds tend to produce more Bottoms that the model forecasts. The effect of nitrogen is not captures in the ^{1}H-NMR spectra.

3.2.6 Coke Yield

The best linear regression model to predict coke has the form for catalyst A:

$$\text{Coke(A)} = 6.157 + 0.332 * (C/O) - 0.764 * H4 - 0.537 * H5 + 2.413 * H6 - 0.586 * H9 + 0.658 * H10 - 0.467 * H12$$

and for catalyst B

$$\text{Coke(B)} = 6.444 + 0.424 * (C/O) - 0.575 * H4 - 0.501 * H5 + 1.364 * H6 + 2.179 * H7 - 1.337 * H8 - 0.308 * H12$$

The coefficient of determination R^2 of the coke model for both catalysts is 0.82. Both coke models for catalyst A and B have different dependence on ^{1}H-NMR spectra ranges. It is interesting to notice that even though both catalysts were deactivated metal free, the feeds with very high level of Vanadium and Nickel gave substantially higher coke yield than predicted from the model. The feed with high level of Vanadium and Nickel is marked as a magenta square in Figure 13. Catalyst B produces more coke than catalyst A except a few cases for feeds with no Vanadium.

3.2.7 Dry Gas yield

Dry gas consists of hydrogen, methane, and ethane products. The best linear regression model to predict dry gas yield for catalyst A has the form:

$$\text{Dry Gas(A)} = -2.18 + 0.158 * (C/O) + 0.908 * H7 - 0.399 * H8 - 0.093 * H9 + 0.034 * H11$$

and for catalyst B

$$\text{Dry Gas(B)} = -2.376 + 0.165 * (C/O) + 1.059 * H7 - 0.474 * H8 - 0.107 * H9 + 0.037 * H11$$

The coefficient of determination R^2 of the dry gas yield model is 0.82 for both catalysts. Based on the model, under the same operating conditions and for the same feed, catalyst B makes always more dry gas than catalyst A. Figures 14 shows Dry Gas yield predicted

from ^{1}H-NMR spectra versus Dry Gas yield observed. For heavy aromatic feeds, green triangles, and feed with high level of Nickel and Vanadium, magenta squares, model under predicts Dry gas yield.

Figure 13. Coke yield predicted from ^{1}H-NMR spectra

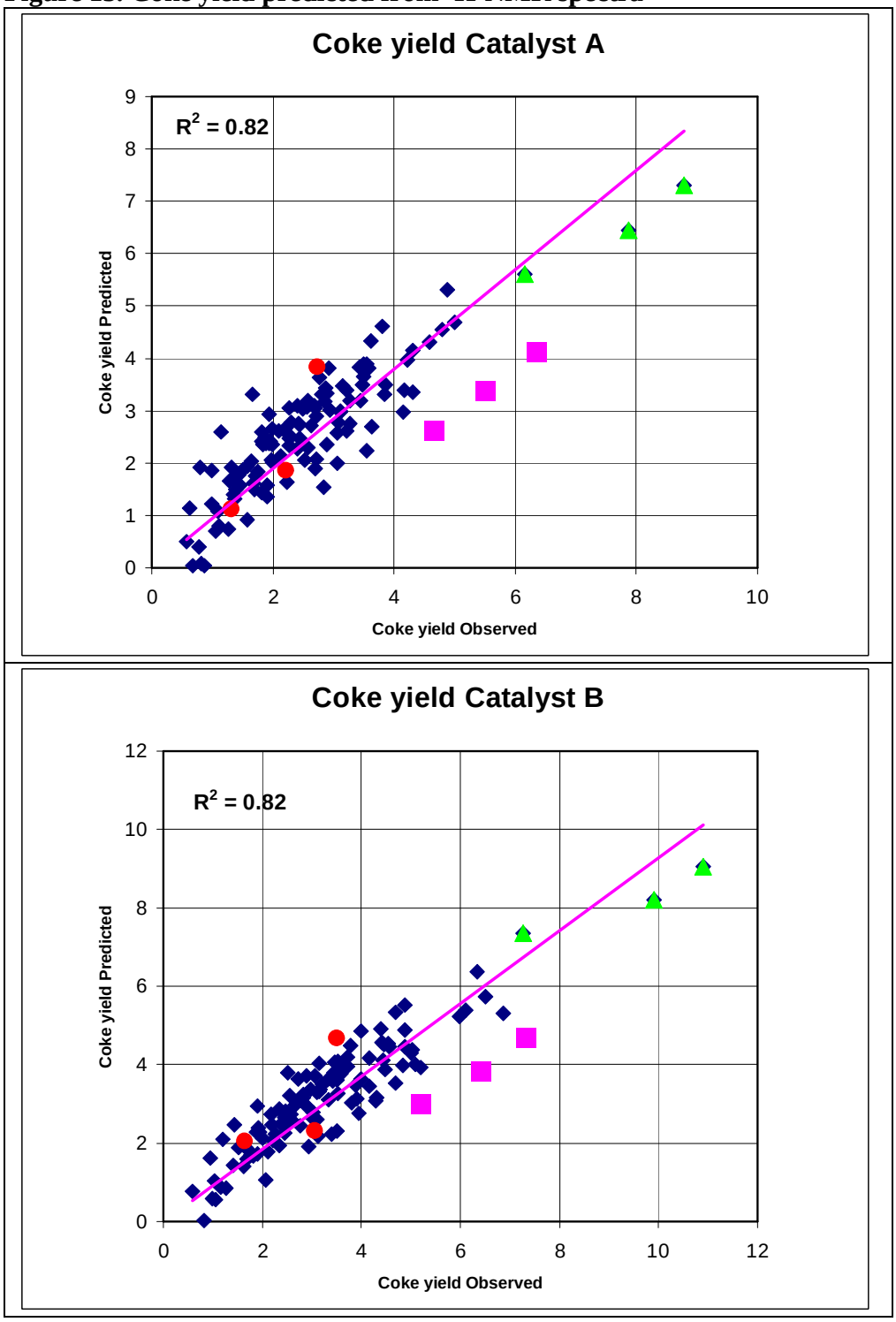
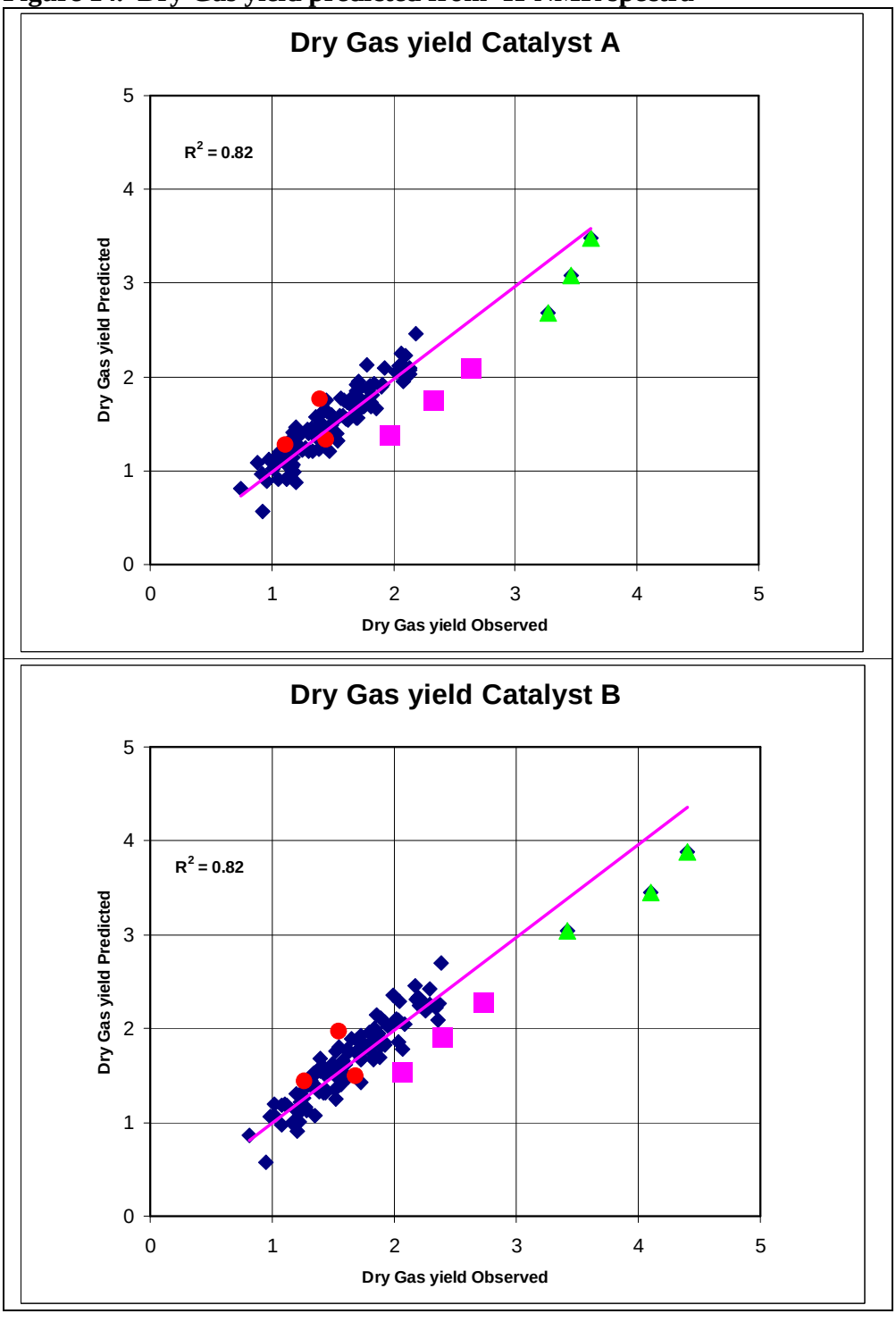


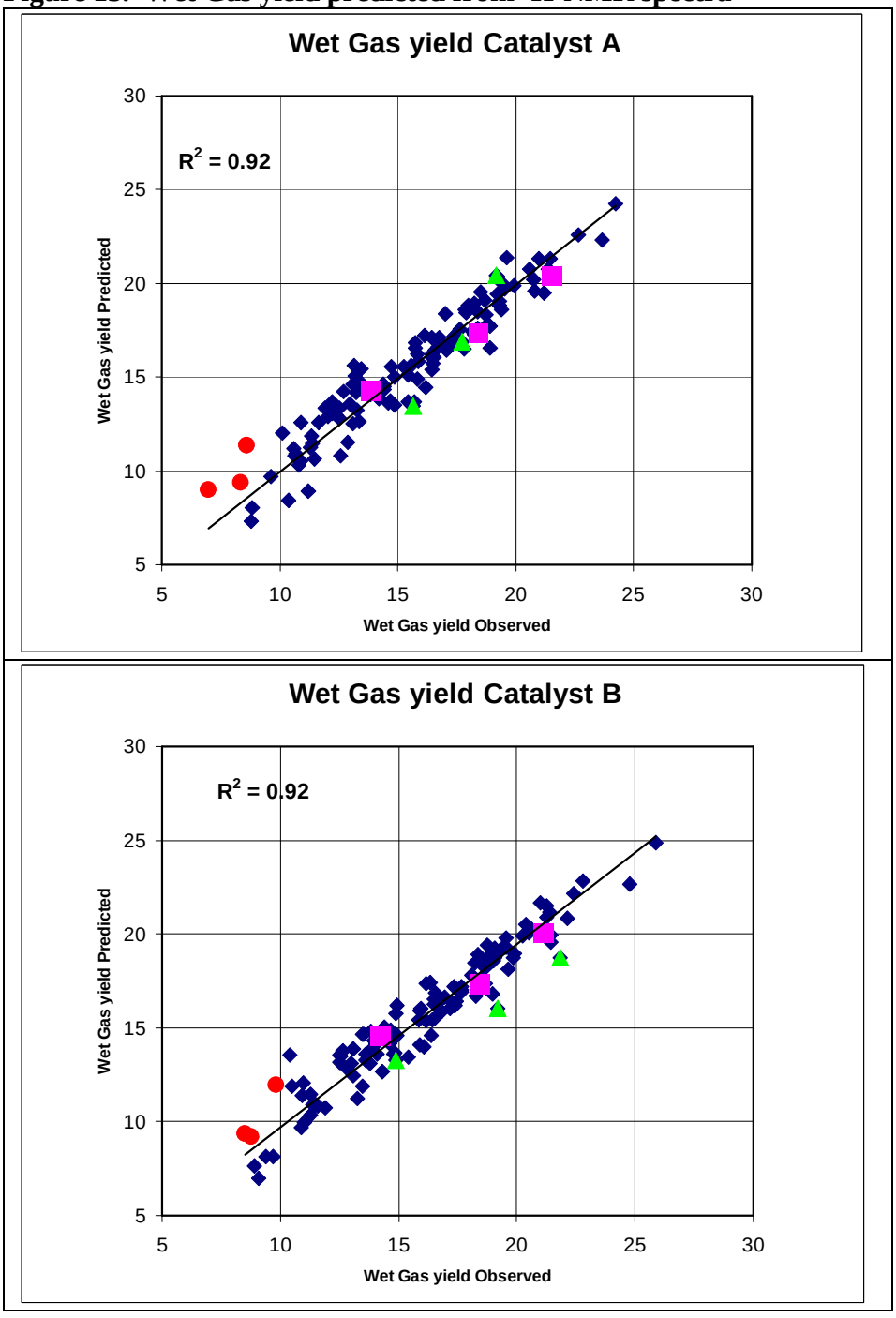
Figure 14. Dry Gas yield predicted from ^{1}H-NMR spectra



3.2.8 Wet Gas yield

Wet gas comprises dry gas and all propane and butane products. The best linear regression model to predict Wet Gas yield for catalyst A has the form:

Figure 15. Wet Gas yield predicted from ^{1}H-NMR spectra



$$\text{Wet Gas(A)} = 16.534 + 1.374 * (\text{C/O}) - 0.593 * \text{H3} + 2.87 * \text{H4} + 1.919 * \text{H5} - 4.574 * \text{H9}$$

While for catalyst B is:

$$\text{Wet Gas(B)} = 17.33 + 1.365 * (C/O) - 0.659 * H3 + 2.865 * H4 + 1.59 * H5 - 4.59 * H9$$

The coefficient of determination R^2 of the Wet Gas yield model is 0.92. Figures 15 shows Wet Gas yield predicted from ^{1}H-NMR spectra versus Wet Gas yield observed.

4. CONCLUSIONS

A feasibility study on application of ^{1}H-NMR petroleum product characterization to predict physicochemical properties of feeds and catalyst-feed interactions has been concluded. The technique can be satisfactorily used to estimate many feed properties as well as catalyst-feed interactions to forecast products yield. There is however limitations that have to be addressed such as inability of this method to include effects of certain type of contaminants such as total nitrogen, nickel and vanadium, etc.

Some of the findings on catalyst-feed interactions have to be properly interpreted taking into account that the catalysts used for the ACE study were deactivated without metals in the laboratory.

5. REFERENCES

[1] Babita Behera, Sidharth S. Ray, I.D. Singh, Structural characterization of FCC feeds from Indian refineries by NMR spectroscopy. Fuel 87(2008):2322-2333.

[2] Daniel Molina V., Uriel Navarro Uribe, and Juan Murgich, Partial Least-Squares (PLS) Correlation between Refined Product Yields and Physicochemical Properties with the ^{1}H Nuclear Magnetic Resonance (NMR) Spectra of Colombian Crude Oils. Energy & Fuels 21(2007):1674-1680.

[3] G.S. Kapur, A.P. Singh, A.S. Sarpal, Determination of aromatics and naphthenes in straight run gasoline by ^{1}H NMR spectroscopy. Part I. Fuel 79(2000):1023-1029.

[4] A.S. Sarpal, G.S. Kapur, S. Mukherjee, A.K. Tiwari, PONA analyses of cracked gasoline by ^{1}H NMR spectroscopy. Part II. Fuel 80(2001):521-528,1.

[5] J. C. Kayser, US Patent 6 069 012 - Versatile fluidized bed reactor, assigned to Kayser Technology, 2000.

[6] D. Wallenstein, R.H. Harding, J.R.D. Nee, and L.T. Boock, Recent advances in the deactivation of FCC catalysts by cyclic propylene steaming (CPS) in the presence and absence of contaminant metals. Appl. Catal. A: General 204 (2000): 89-106.

[7] K. Van Nes, and H.A. van Westen, Aspects of the Constitution of Mineral Oils, Elsvier, New York, N.Y., 1951.

[8] J. Smittenberg, and D. Mulder, Relations between refraction, density, and structure of series of homologous hydrocarbons. I. Empirical formula for

refraction and density at 20^{o} of n-alkenes and n-alpha-alkenes. Rec. Trav. Chim., 67 (1948):813-825, 826-838.

[9] K.M. Watson, E.F. Nelson, and G.B. Murphy, Characterization of Petroleum Fractions. Ind. Eng. Chem. 27(1935):1460-1464.

[10] E. Hirsch, Relations Between Molecular Volume and Structure of Hydrocarbons at 20 oC, Anal. Chem., 42(1970):1326-1329.

[11] M. R. Riazi, and T. E. Daubert. Prediction of the Composition of Petroleum Fractions. Ind. Eng. Chem. Proc. Des. Dev. 19(1980):289-294.

[12] Standard Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method, ASTM D3238-95(2005).