

THE VALIDATION OF AN ON-LINE NUCLEAR MAGNETIC RESONANCE SPECTROMETER FOR ANALYSIS OF NAPHTHAS AND DIESELS.

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ABSTRACT

This paper discusses the efforts to commission and validate an online Nuclear Magnetic Resonance Spectrometer [NMR] for the analysis of heavy feedstock to a cracking plant. Reference will be made to ASTM D3764 – Standard Practice for Validation for Process Stream Analyzers (1). Results from laboratory analyses of standards and plant samples will be presented.

INTRODUCTION

The cracking of heavy feedstock to produce olefins and other downstream derivatives can be optimized by controlling many plant parameters such as Coil Outlet Temperatures, Hydrocarbon to Steam Ratio, Flow Rates, Pressures, etc. These parameters can be varied based on kinetic and thermodynamic models to increase the quantities of the more economically preferred products. Several commercial software packages are available to the plant to assess all input information and tune the furnace cracking conditions to afford these optimal conditions. One important piece of information for the optimizing software is the exact make up of the furnace feedstock. Plants that crack gases such as ethane, propane, and butane can effectively analyze their feedstock and furnace effluent by gas chromatography. The products of such plants are not complicated and would not benefit from optimizing programs. However, heavier feedstock such as Natural Gasoline, Naphtha, Condensates, and Diesels can have a widely variable composition, and as such the furnace yields can vary in their components and concentrations. This is even more the case if the plant receives many different types of feedstock from the spot market and local refineries. The cracker facility at Corpus Christi, TX installed an NMR (2) in 2002 for feedstock analysis to provide detailed information to the Spyro / RT-Opt plant optimization package (3).

PROJECT REQUIREMENTS

This project sought bids that would provide as a minimum the following information.

- Normal Paraffins: C4, C5, C6, C7, C8, C9, C10, C11, C12+, and total
- Isoparaffins: C4, C5, C6, C7, C8, C9, C10, C11, C12+, and total
- Naphthenes: C5, C6, C7, C8, C9, C10, C11, C12+, and total
- Aromatics: C6, C7, C8, C9, C10, C11, C12+, and total
- D86 Distillation: Initial Boiling Point [IBP], T10, T50, T90, and End Boiling Point [EBP].
- D2887 Simulated Distillation: Initial Boiling Point [IBP], T10, T50, T90, and End Boiling Point [EBP].
- % Hydrogen
- Specific Gravity

HARDWARE

LABORATORY EQUIPMENT

The lab experiments were carried out on an Agilent (HP) 6890 with split inlet and flame ionization detector. The column used is a 50m x 0.20mm id crosslinked methyl siloxane 0.5um film thickness (HP PONA). The method is based on ASTM Method D6733, Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 50-Meter Capillary High Resolution Gas Chromatography. Software from the Institut Francais Du Petrole (IFP) called Carburane was used to identify components in the GC analysis and to produce the detailed hydrocarbon report.

In addition to the above, an HP 5973 GC/Mass Spectrometer system was used to verify peak identification. The system consists of an HP 6890 GC with split inlet and HP5973 mass spectrometer featuring a hyperbolic quadrupole mass filter. Software from SINTEF Applied Chemistry in Oslo, Norway called SI-PIONA is used to help identify peaks using a combination of two libraries, a library of mass spectra and a retention library. The GC column used for this application is a 100m x 0.25mm id crosslinked methyl siloxane with a 0.5um film thickness (Chrompak CP-SIL PONA CB).

Hydrogen content was measured on a Bruker MiniSpec benchtop NMR. D86 was run on standard lab distillation equipment.

ANALYZER HARDWARE

Two process headers were tapped, and an insulated 1/4" dual tubing bundle run about 200 feet to an existing analyzer house. The sample conditioning cabinet which is located on the outside wall of the house consists of manually activated block and bleed valves, coolers with temperature switches, stream switching valves, flow control, fast speed loops, and a manual sample collection point. A switch was built into the programmable logic controller [PLC] logic to allow the stream switching to be halted while a sample was collected, to ensure the timestamp and stream of the sample could be correctly labeled. The analyzer itself has dual 3-way block valves to provide a constant by-pass while the measurement is made on a static sample. The analyzer is contained in a free standing Class 1 Div 2 stainless steel

enclosure with a built in air conditioner for the on-board electronics and computer. The sample measurement probe is isolated in a temperature controlled box within the enclosure. A remote PC in the analyzer control room is linked by PC AnyWhere / Ethernet for viewing all diagnostics and results. Separate Modbus connections link direct to the Distributed Control System [DCS] for plant use. The sample return point was close to the analyzer house, just downstream of the cracking furnaces, with magnetically coupled pumps to provide the required by-pass flow rate. However, the start-up of the NMR was delayed when the pumps were found to be undersized and constantly decoupling. A review of the situation caused a relocation of the return point to a lower pressure process entry upstream of the furnaces (albeit a longer tubing run), thus negating the need for the pumps. This also increased the economic value of the feedstock in the fast speed loop (60 gallons per hour).

VALIDATION

COMMERCIAL VALIDATION LIMITS

Based on careful examination of the lab paraffins, isoparaffins, naphthenes, and aromatics [PINA] repeatability, and ASTM methods D86 (4) and D2887 (5), a set of validation limits for the PINA and distillation parameters was finalized. These limits could theoretically be equated to the analyzer reproducibility in that the results from the analyzer and the lab for the same sample should not exceed these limits in more than 1 case in 20 (95 % confidence limit). The limits are shown in Table I.

TABLE I. COMMERCIAL VALIDATION LIMITS FOR PINA AND DISTILLATION PARAMETERS.

Parameter	Validation Limits [wt%]
n-hexane	0.80
n-nonane	0.20
Total n-paraffins	1.00
i-hexane	1.00
i-nonane	0.40
Total i-paraffins	0.60
cyclohexane	0.20
C9-naphthene	0.30
Total naphthenes	0.50
Benzene	0.20
C9-aromatics	0.20
Total Aromatics	0.30
D86 [IBP, T10, T50, T90, EBP]	14 °F
D2887 [IBP, T10, T50, T90, EBP]	9 °F
Density	0.003 g/ml

LAB VALIDATION

The modeling process for the online NMR relies exclusively on the lab results of plant samples. Therefore it is imperative that the lab analyses are as accurate and precise as possible. The first step in the validation of the Online Analyzer is therefore to accredit the lab. To this end a gravimetric standard (6) was purchased and analyzed on six non consecutive days. This exercise essentially establishes the precision statement (7) for the applicable test method since the lab test is not routine. The components and results for the standard are shown in Table II.

TABLE II. COMPONENTS IN LABORATORY GRAVIMETRIC STANDARD.

Component	Certified [wt %]	Measured Average [wt%]	% RSD [n=6]	Component	Certified [wt %]	Measured Average [wt%]	% RSD [n=6]
n-pentane	2.354	2.18	1.06	benzene	2.359	2.31	1.22
n-hexane	2.374	2.33	0.51	toluene	2.465	2.42	0.81
n-heptane	2.399	2.38	0.14	ethylbenzene	2.420	2.42	0.43
n-octane	2.367	2.38	0.16	p-xylene	3.300	3.28	0.53
n-nonane	2.389	2.43	0.34	propylbenzene	2.354	2.37	0.21
n-decane	2.394	2.44	0.51	cumene	1.833	1.84	0.20
n-undecane	2.367	2.47	0.67	3-ethyltoluene	1.910	1.92	0.26
n-dodecane	2.394	2.35	0.64	1,2,4- trimethylbenzene	1.751	1.79	0.25
isopentane	1.888	1.74	1.03	1,3,5- trimethylbenzene	1.439	1.46	0.26
2-methylpentane	1.675	1.62	0.42	n-butylbenzene	2.407	2.45	0.43
3-methylpentane	1.738	1.70	0.39	isobutylbenzene	2.214	2.26	0.33
2,2-dimethylbutane	1.572	1.52	0.44	1,2,4,5- tetramethylbenzene	1.245	1.23	0.55
2,3-dimethylpentane	2.843	2.82	0.16	n-pentylbenzene	2.399	2.45	0.61
2,4-dimethylpentane	1.790	3.68	0.28	1-pentene	2.213	1.99	1.31
2,2,4-trimethylpentane	2.231	4.62	0.18	1-hexene	2.399	2.29	0.66
cyclohexane	2.367	2.32	0.42	2,3,3-trimethyl-1- butene	1.073	1.03	0.20
methylcyclohexane	2.367	2.36	0.22	1-octene	2.399	2.34	0.11
ethylcyclohexane	2.399	2.40	0.22	2-methyl-1-heptene	1.310	1.29	0.14
propylcyclohexane	2.367	2.40	0.28	1-nonene	2.379	2.38	0.33
n-butylcyclohexane	2.347	2.40	0.45	1-decene	2.379	2.37	0.52
n-pentylcyclohexane	2.379	2.45	0.61	1-undecene	2.420	2.50	0.70
decalin total	1.959	1.99	0.50	dodecene	2.379	2.32	0.67

The % relative standard deviations are all extremely low, showing the excellent repeatability of the chromatographic method. Although this gravimetric standard had many of the components that are expected to be found in a naphtha or condensate, the proportions of those constituents are not similar. Therefore a plant sample was also analyzed on six non consecutive days, and the variance compared to the gravimetric standard by the F-Test (8-10) to determine if a significant difference existed between

analyzing standards and plant samples by the analytical method. The results for the plant samples and the corresponding F-Test values are shown in Table III.

TABLE III. RELATIVE STANDARD DEVIATIONS AND F-TEST RESULTS FOR TWO PLANT SAMPLES

Critical F = 5.05 for a limited Reference Set						
	Naphtha Average	% RSD [n=6]	F result	Condensate Average	% RSD [n=6]	F result
n-c4	1.27	0.70		3.91	0.85	
n-c5	10.95	0.60	8.08	9.37	0.55	5.05
n-c6	7.81	0.35	5.19	7.27	0.39	5.88
n-c7	5.05	0.08	1.42	6.03	0.28	24.92
n-c8	4.25	0.31	11.95	4.42	0.35	16.00
n-c9	3.92	0.40	3.63	3.07	0.51	3.57
n-c10	1.85	0.49	1.93	2.13	0.70	1.44
n-c11	0.13	0.55	544.47	1.42	0.81	2.09
n-c12+				2.36	0.92	2.06
Total n-paraffins	35.24	0.18	7.50	40.08	0.26	20.65
l-c4	0.09	5.96		0.72	1.12	
l-c5	5.78	0.64	4.19	6.68	0.59	4.80
l-c6	7.53	0.41	2.55	6.39	0.41	1.84
l-c7	4.78	0.11	6.64	6.21	0.28	1.64
l-c8	5.07	0.23	2.02	6.33	0.33	6.57
l-c9	4.95	0.66		4.25	0.31	
l-c10	3.49	0.45		3.74	1.02	
l-c11	0.50	0.74		1.67	0.88	
l-c12+				2.35	2.80	
Total l-paraffins	32.19	0.08	4.56	38.34	0.14	1.01
cyclopentane	0.66	0.45		0.28	0.62	
me-cyclopentane	2.00	0.29		0.67	0.43	
cyclohexane	1.71	0.21	7.37	1.36	0.38	3.58
methylcyclohexane	3.35	0.12	1.79	2.59	0.29	2.09
Other c7-Nap	2.13	0.14		1.19	0.29	
c8-Nap	5.66	0.62	42.69	2.02	0.92	12.21
c9-Nap	5.56	0.34	7.69	2.45	0.49	3.24
c10-Nap	1.93	0.93	1.06	1.26	1.84	1.59
c11-Nap	0.30	6.39	1.70	0.87	8.38	23.89
c12+Nap				0.84	11.37	
Total Naphthenes	23.30	0.24	2.33	13.54	0.97	13.20
Benzene	1.30	0.29	53.71	2.34	0.40	9.09
Toluene	1.25	0.17	87.46	1.00	0.30	42.95
Ethylbenzene	0.33	0.39	68.55	0.13	0.43	367.22
Xylenes	2.28	0.36	4.38	1.01	0.41	17.50
c9-Arom	3.16	0.47	2.01	1.13	1.35	1.94
c10-Arom						
c11-Arom				0.52	4.30	
c12+Arom	0.95	1.70		1.71	2.99	
Total Aromatics	9.27	0.33	3.49	7.84	0.67	1.17

The components of the gravimetric standard have been relabeled to fit the descriptions required for the online NMR. The critical F value for a limited reference set [five degrees of freedom] is 5.05 and many of the test parameters pass this test. For those parameters that do not pass the F-Test, if an assignable cause can be found, then no corrective actions need be taken. This was the case for all parameters that failed the F-test (e.g. very low concentrations that result in high standard deviations), and the method was therefore deemed suitable. An examination of the % relative standard deviations [RSD] for all components shows very low values, except for the higher carbon numbers where integration starts to get difficult. Based on these test results, the lab was considered more than adequate in its ability to provide high quality data for input to the modeling process.

ANALYZER VALIDATION

ASTM Method D3764 was cited by the analyzer vendor as the vehicle to be used in the commercial validation process of the analyzer. D3764 describes the steps to be taken to compare lab results with analyzer results, and the statistical methods employed to decide if the two results are significantly different or not. It was found that this method could only be used as a guide for the actual process finally agreed to by the customer and the vendor. Section 4 of ASTM D3764 refers to two procedures that can be used in the validation process. The Reference Sample Procedure involves a laboratory calibrated sample that is introduced into the analyzer and results compared. The Line Sample Procedure involves withdrawal of samples from the analyzer system, with subsequent comparison of a lab result with the result of the analyzer at the time of sampling. The constraints of time and distance forced the latter procedure onto the validation process.

RESULTS

Existing models developed at existing NMR users for PINA and D86 were installed on the analyzer after all initial hardware situations were corrected. The modeling was done by PLS (11). D2887 models were developed with new plant data since these had not been previously established. The process of collecting lab data for incorporation into the training set began by catching samples in stainless steel cylinders, and synchronizing the timestamp with the NMR measurement. The samples were shipped in the cylinders from the plant in Corpus Christi, TX to the testing lab in Channelview, TX. Early data showed that the existing models would require input from the new installation to improve the predictions. This is illustrated in Table 4.

TABLE 4. FIRST RESULTS FROM OLD AND NEW MODELS.

Model	Sample			Total			Total
	Number	n-c6	n-c9	n-paraffins	i-c6	i-c9	
Ver1	651	17.12	-0.01	43.16	15.82	-0.68	32.47
Ver1	652	18.57	0.00	45.40	16.09	-0.87	31.32
Ver1	663	18.73	-0.03	46.11	15.84	-1.04	30.74
Ver1	667	14.85	-0.16	41.46	14.23	-0.81	32.54
Ver1	670	18.81	0.69	45.36	15.52	0.08	32.84
Ver2	656	7.55	1.85	35.79	10.57	2.27	36.36

Ver2	661	7.42	1.57	35.22	9.75	2.82	35.32
Ver2	662	7.60	2.10	34.97	10.50	1.95	37.05
Ver2	669	6.97	1.64	34.01	9.96	2.39	37.48
Model	Sample Number	cyclo hexane	C9-Nap	Total Napthenes	Benzene	C9-Arom	Total Aromatics
Ver1	651	4.35	0.57	14.52	2.64	-0.45	5.16
Ver1	652	4.60	0.44	13.60	2.59	-0.31	4.68
Ver1	663	4.71	0.47	13.05	2.48	-0.20	4.32
Ver1	667	5.70	0.95	16.48	2.64	-0.14	5.26
Ver1	670	3.56	1.10	12.20	2.27	0.00	4.91
Ver2	656	2.16	2.05	17.66	2.82	1.05	9.70
Ver2	661	2.20	2.46	17.19	2.57	1.34	9.89
Ver2	662	1.75	1.84	15.35	2.98	0.90	10.16
Ver2	669	1.68	2.30	14.95	2.66	1.22	9.83

Results from model Version 1 did not accurately predict the validation parameters, but the addition of results from the samples caught at the new facility into the training set improved the results markedly.

The first set of models for the D2887 and D86 were installed after about 3 months of data collection, comprising approximately 60 samples. The results for T50 and T90 were found to be the most robust. This is not surprising, since the feedstock mixture of heavy and light materials caused wide variation in the initial boiling points [IBP] and end boiling point [EBP]. D86 apparatus cannot handle heavy tails very well, and the GC SimDist D2887 method was set up for diesels. The transition from a light condensate to a diesel is captured very well by the NMR distillation predictions, and they match the lab results quite closely as seen in Figure 1. Trend lines from the NMR for density, total i-paraffins, and total aromatics are also shown in Figure 2.

CONCLUSION

An NMR was successfully installed at the Equistar Corpus Christi plant and is being used to characterize naphthas, condensates, and diesels. The predictions are being used in conjunction with a Whole Plant Optimization software package to run the furnaces to produce higher yields of more economically favorable hydrocarbons. The financial impact of the analyzer has not yet been established but is expected to be > \$1 million / year.

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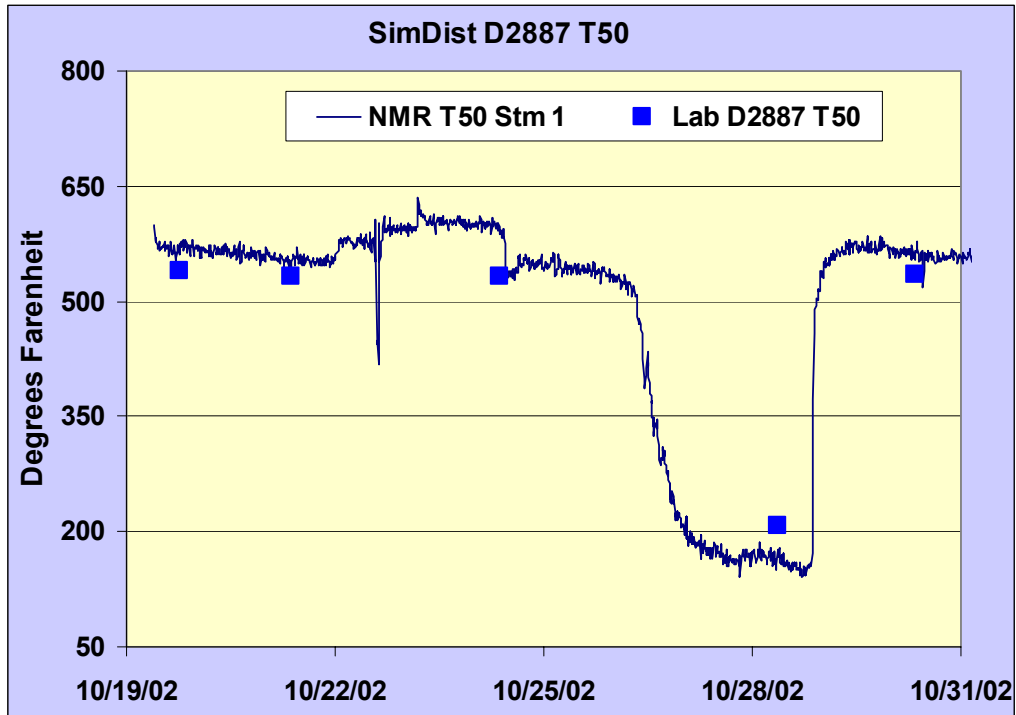


FIGURE 1. SIMULATED DISTILLATION T50 PREDICTIONS FEEDSTOCK TRANSITION.

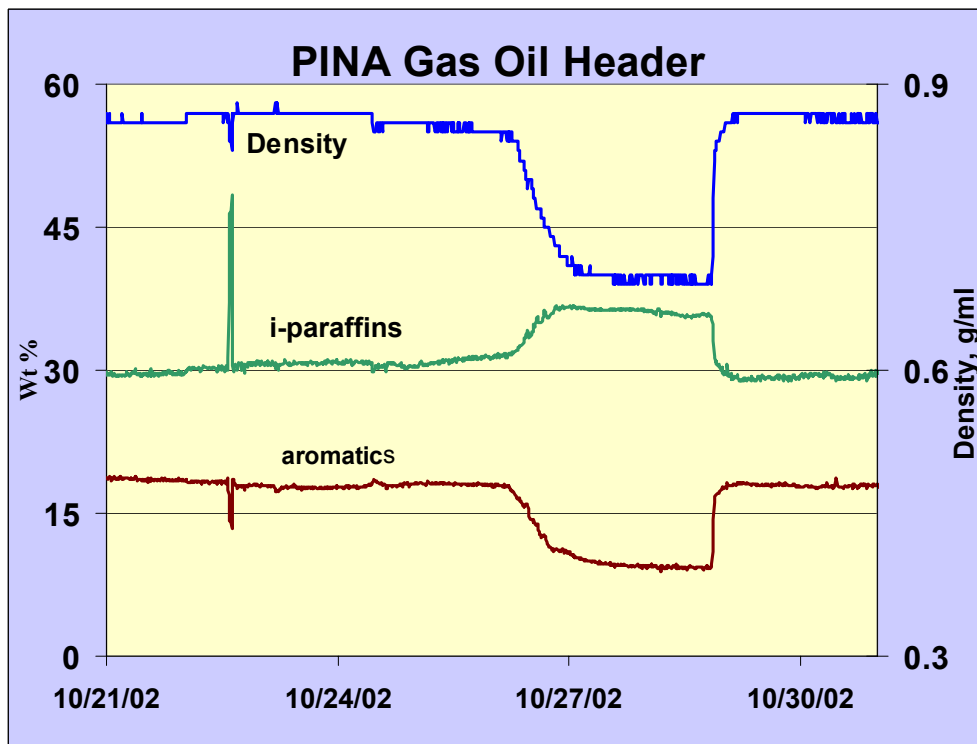


FIGURE 2. PREDICTIONS FOR TOTAL AROMATICS, ISOPARAFFINS, AND DENSITY.

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4. ASTM D86-00a Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure
5. ASTM D2887-02 Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography
6. Gravimetric Standard
7. ASTM D3764 Section 3.1.12. This gravimetric standard can also be described as the Reference Sample , section 3.1.14.
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