Product Differentiation for Profit Maximization in FCC Unit Operations

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1. Abstract

The Fluid Catalytic Cracking process, since its discovery in the early 1920s, became an inherent part of petroleum refinery operations. It plays an important role in upgrading feedstock, which typically comprise of high molecular weight hydrocarbons, to lower molecular weight products like Gasoline, Diesel, and LPG. In addition to volumetric expansion, these products enjoy also higher value markup against their initial raw materials. While the chemical composition of the feedstock affects the slate and quality of major FCC products, the FCC catalyst and unit operating conditions unlock the feedstock potential to produce those valuable products thus influencing the whole refinery economics. Understanding complex interactions between the feedstock, the catalyst, and FCC unit operating conditions is the key to proper catalyst selection and optimum unit operation. As the market conditions fluctuate over time so does the economic value of major feed cracking products that may require adjustment to the catalytic system and/or operating conditions to achieve a new operational and financial optimum. The same concept applies when the FCC feedstock's properties change since they are blends of virgin and preprocessed crude oils and refinery streams of low economic value.

To understand and study those intricate relations, over a hundred FCC feeds, originating from diverse geographical locations around the world, covering a wide range of properties, and including ones that require special initial preprocessing, were assembled. Extra effort was made to assure that this collection represents the type of feeds that are used by the industry today, including North American shale oil. All feeds were thoroughly characterized for physical and chemical properties using standard industry methods [1], and they were evaluated in the ACE apparatus against three families of commercial FCC catalysts using a range of severities (cat-to-oil ratio from 0 to 100, and reactor temperatures from 778 to 817 K). These catalysts were laboratory-deactivated using the Cyclic Propylene Steaming, a metal-free deactivation protocol. The rationale for using metal-free deactivation, besides simplifying the analyses, was to focus on the catalyst-feed interactions during the cracking process. Cracking products were identified and thoroughly characterized.

All these experimental data were used to develop a model that allows for predicting major cracking product yields in the ACE unit while taking into account feed properties and operating conditions. Based on a snapshot of market prices of major cracking products, different market scenarios were simulated and optimum operating conditions to maximize operation economics were discussed. This paper examines also the effect of adding low cost and low quality opportunistic feeds to the FCC unit feed blend on operations economics. At the end it provides helpful guidelines for FCC engineers on the effect of feed properties on the FCC unit operations, process optimization, and profit maximization.

2. Introduction

Fluid Catalytic Cracking process is an important part of refinery operations that converts raw materials into valuable products. Because of its robustness, it can process feeds with a wide range of properties,

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blended with recirculating refinery streams of low economical value thus upgrading them to higher market value products such as Gasoline, Diesel, and LPG. While the hydrocarbon cracking process in the FCC unit follows the thermodynamic and reaction kinetic principles, there is always some freedom to control the operating conditions and the catalyst properties and activity to affect the slate and quality of the products. The individual product classes are based on a boiling point range. The specification of those product classes depends on regions and countries. In the US, gasoline fraction covers liquid hydrocarbons with boiling temperature below 221°C (430 ^{o}F), Diesel is from 221 to 370°C (430 ^{o}F to 700 ^{o}F), and LPG comprises C_3 and C_4 hydrocarbons that can be easily liquefied under normal temperature by applying only moderate pressure.

During the cracking process, there is a continuous transformation of hydrocarbon molecules from the feed into more molecules (molar expansion) of different hydrocarbons with a lower molecular weight. As the cracking process progresses, the molecular weight distribution and corresponding boiling temperature distribution shift to lower values changing the distribution of individual products and their quality. Because each of the products has a different market value depending on a particular geographic location that may also change over time, the FCC unit optimum operation is not constant as well. The individual product yield and quality are nonlinear with respect to conversion that makes the optimization process not trivial.

In this paper, we studied the intricate relationship between the raw materials quality (feeds) and FCC unit operating conditions (riser temperature, and catalyst circulation rate), and the quantity and quality of major products. Cracking experiments were conducted using ACE apparatus, and the experimental data was used to develop a model capable of predicting major cracking products yields and qualities based on just the physicochemical properties of feeds and the reaction severity (cat-to-oil ratio and reactor temperature).

3. Experimental Conditions

Over a hundred FCC feeds, originating from diverse geographical locations around the world, covering a wide range of properties, and including ones that require special initial preprocessing, were assembled. All feeds were thoroughly characterized for physical and chemical properties using typical industry methods. Table 1 shows the range of feed properties used in this work.

Feeds were evaluated in the ACE apparatus against three different families of Grace commercial FCC catalysts. Catalysts were deactivated in laboratory using a metal-free Cyclic Propylene Steaming protocol [2]. A range of experiments, some of them nonstandard, were performed to develop data covering a full range of conversions and operating severities. Testing conditions used in the study were:

- Reactor temperature from 504°C to 543°C (940 ^{o}F to 1010 ^{o}F)
- Feed injection rate 3 [g/min]
- Feed injection time 30 [s]
- Catalyst-to-oil ratio 0 to 100

Feed cracking products were characterized using RGA, SIMDIS, and PIONA system. Coke was analyzed by LECO.

Table 1. Properties of the feeds used in this study.

Property	Minimum	Maximum	Average
Api	11.68	32.67	21.21
Sulfur	0.002	3.61	1.28
Total Nitrogen	0.00	0.35	0.20
Basic Nitrogen	0.00	0.11	0.06
Conradson Carbon	0.07	5.34	1.77
Refractive Index	1.48	1.57	1.52
Average Molecular Weight	334	453	376
$C_{Aromatic}$	13.30	44.90	27.44
$C_{Paraffinic}$	50.90	67.70	57.31
$C_{Naphthenic}$	3.20	21.40	15.26
K-factor	11.06	12.24	11.54
TB50, °C	394	512	429
Correlation Index	24.36	73.26	52.33
Hydrogen Content, wt%	10.47	13.43	11.65

4. Results and Discussions

Gasoline is one of the most desirable products of the feed cracking process in the FCC operations. To analyze typical Gasoline yield, data was plotted against refinery conversion[2] at two different reactor temperatures 504°C (940 °F) and 543°C (1010 °F), see Figure 1. Looking at the 543°C (1010 °F) isotherm, it becomes obvious that as the conversion initially increases the Gasoline Yield increases too. The curve, however, has a maximum that is called Maximum Potential Gasoline Yield (MPGY) at the corresponding conversion called Maximum Potential Gasoline Conversion (MPGC). At the conversion higher than the MPGC point, the gasoline yield goes down.

While the shape of gasoline yield isotherm at 504°C (940 °F) curve looks similar to 543°C (1010 °F) isotherm, it does not have a clear maximum. Because of the limitations of the standard testing procedure in the ACE apparatus, the MPGY point cannot be found experimentally in this case. In this study we used statistical models and correlations that allow extending of those isotherms beyond conversions tested experimentally. Those statistical models and correlations were described elsewhere [1]. While intuitively making more Gasoline makes sense, it becomes more complicated when Gasoline quality is also considered. In the same graph, MON isotherms are represented by dash lines. The colors of curves and shapes of experimental point markers are the same for the same temperature isotherms. The MON isotherms monotonically rise with respect to conversion. For this study, we assumed a linear price model for Gasoline MON with respect to MON values that reflects the Gasoline of different octane number retail prices in US markets. Based on this assumption, the maximum value of Gasoline can be found by finding the maximum of the product (Gasoline Yield * Gasoline MON) with respect to conversion, see Figure 2. Again, the maximum here can be easily found either graphically or by

[2] By definition, conversion is calculated as**: Conversion = 100 – LCO - Bottoms**

interpolation for the 543 °C (1010 °F) isotherm. There is, however, a problem with 504°C (940 °F) isotherm because the maximum is outside of the experimentally defined domain.

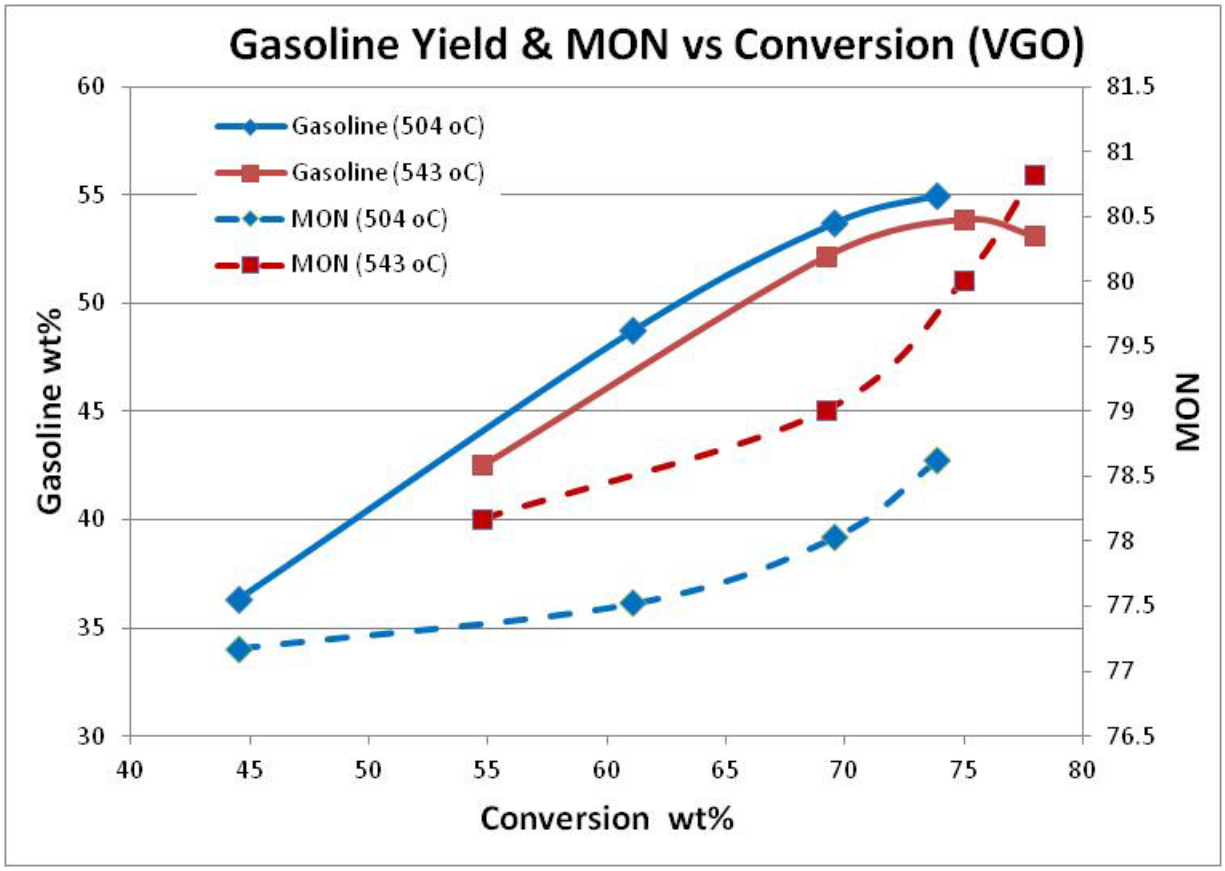

Figure 1 Gasoline yield and MON vs. Conversion using typical VGO feed in ACE test

Figure 3 demonstrates the point why simple extrapolation may not work to find MPGY point if experimental data does not cover the over-cracking region. In this figure, the blue crosses represent experimental data points from ACE experiments conducted at reactor temperature of 504°C (940 °F). The dotted blue line is the best trend line for the experimental points. Unfortunately such a trend line does not have a maximum in the range of reasonable conversions. Based on 298 experimental points, a correlation-based model was developed that captured the relations between feed and catalyst properties, and cracking conditions, and the yields and properties of major cracking products.

Some of the catalyst-feed experiments covered the over-cracking region that the model generalized and used for educated predictions. The blue line in the Figure 3 shows the model predictions for the Gasoline Yield 504°C (940 °F) isotherm. The maximum gasoline yield can easily be determined using this model. There are two dash lines in Figure 3, the red line representing the upper and the blue one for lower confidence limit for the experimental data. The blue solid line, representing the Gasoline Yield model prediction, lies in between those two confidence limit lines for the ACE experimental data, which provides additional assurance for the model quality.

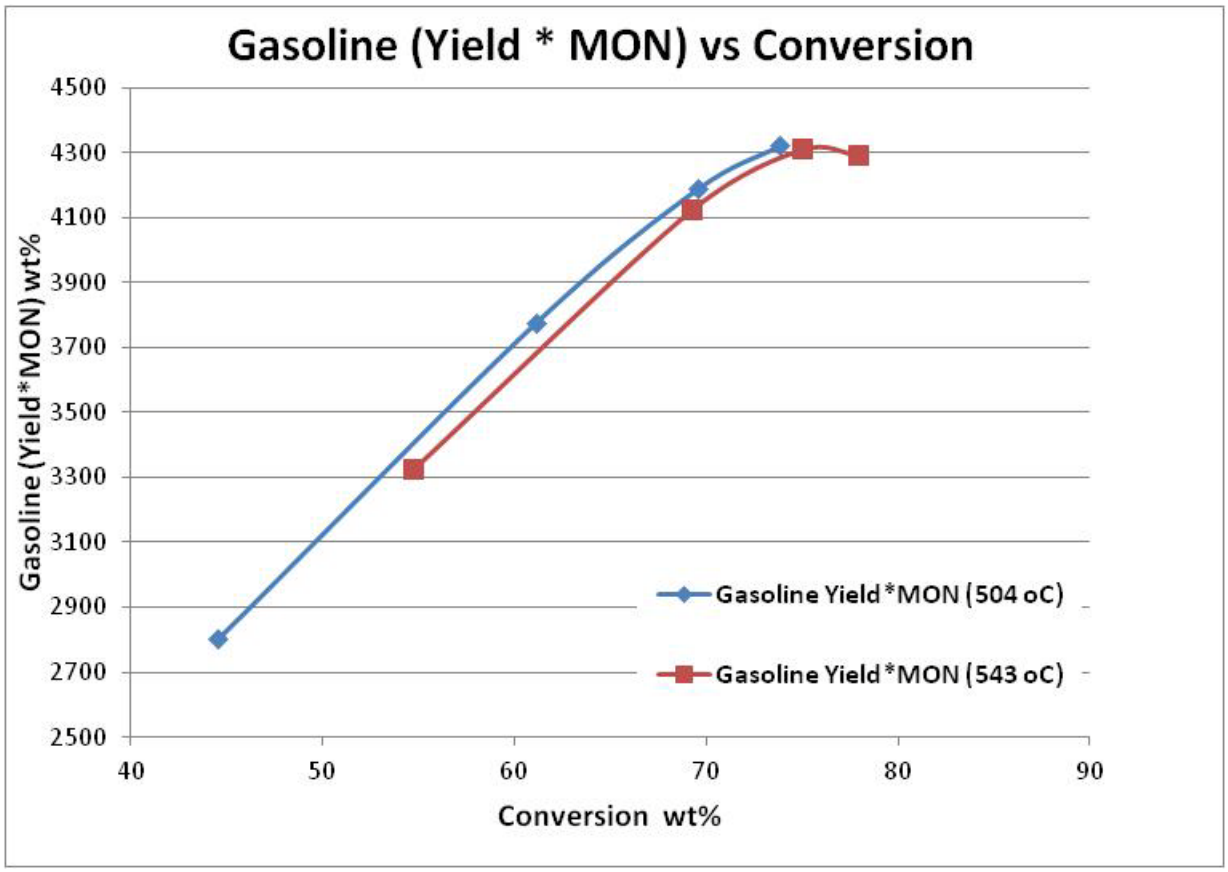

Figure 2 Gasoline (Yield * MON) vs. Conversion using typical VGO feed in ACE test

LCO is by volume and value the second most valuable product, after Gasoline, coming out of the FCC cracking operations. Figure 4 shows Gasoline and LCO Yields versus Conversion for a typical VGO feed. The solid lines correspond to Gasoline and the dash lines represent LCO. The 504°C (940 ^{o}F) and 543°C (1010 ^{o}F) isotherms are plotted using blue and red colors respectively. While finding the MPGY point was already discussed, the same method may not be applicable for the LCO Maximum Yield.

In typical cases, the conversions for LCO maximization are too low to be studied using the ACE apparatus. Because the experimental data are too far from the region where LCO has a maximum, the correlation-based statistical model should be used with caution. In such a case, a lumping scheme model is much better suited to extrapolate experimental data to the regions beyond the experimental capabilities of the ACE unit [3, 4, 5].

Because both the Gasoline and LCO Yields at the lower reactor temperature of 504°C (940 ^{o}F) are higher than those at the 543°C (1010 ^{o}F), only the 504°C (940 ^{o}F) isotherm will be analyzed for the yield maximization. In Figure 5, the ACE experimental points of LCO Yield at 504°C (940 ^{o}F) are represented by blue crosses. The correlation model of LCO Yield, shown here by solid blue line, was used to extrapolate the yield experimental values to the low conversion region. From the correlation model, the maximum LCO Yield can be found, marked in Figure 5 by red circle.

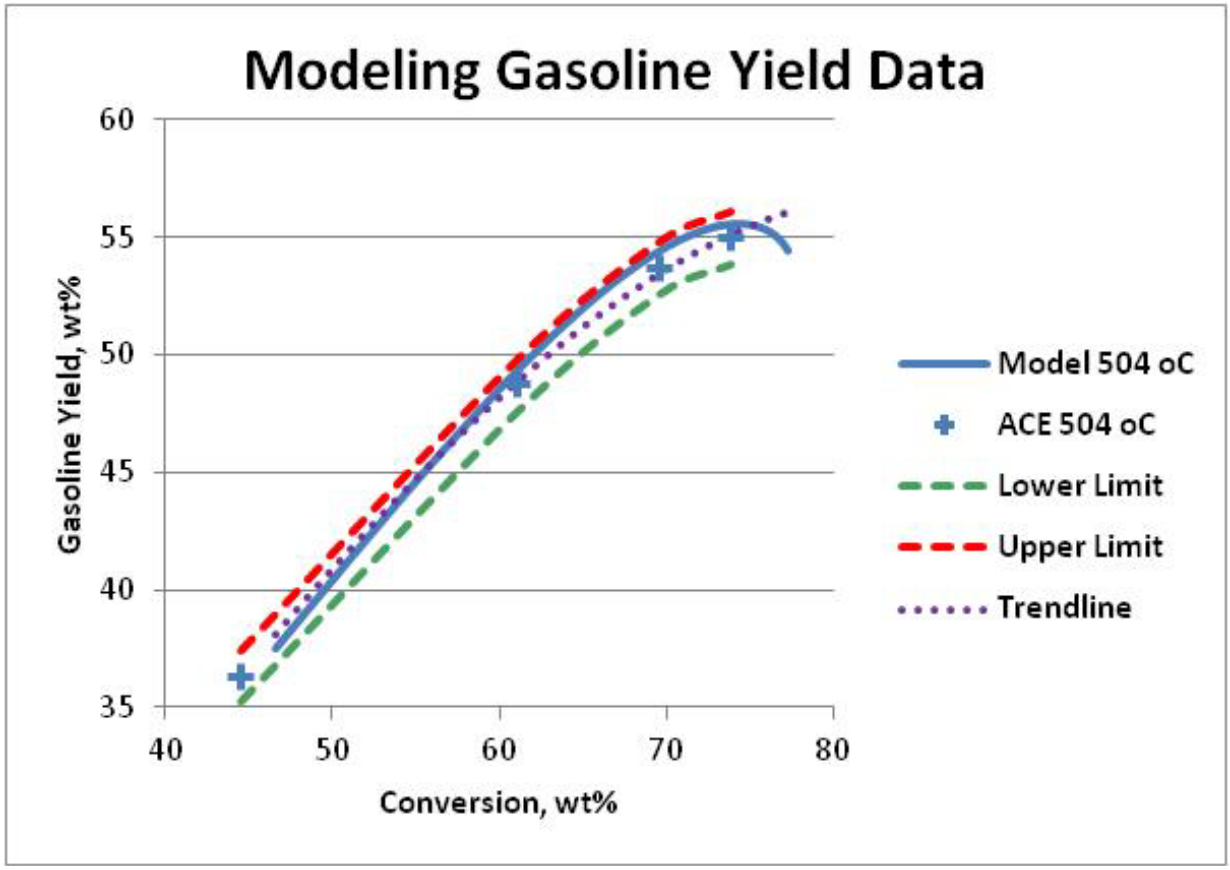

Figure 3 Application of statistical model for Gasoline Yield data extrapolation

The findings for Gasoline and LCO maximization were put together in Figure 6 where solid markers were used for experimental values of Gasoline, LCO, and Gasoline + LCO yields. Lines were used for model predictions and empty circles marked the maximum yields for corresponding products. It becomes clear that lower conversion favors LCO production, and that higher conversion is beneficial for Gasoline production. Depending on the relative prices of Gasoline and LCO, the maximum value for both is, of course, in between the individual maximum points.

In Figure 6, the blue circle represents the maximum of the sum of Gasoline and LCO yields assuming that both products have the same unit value. Again depending on the relative value of both products, the optimum conversion point will move on the conversion scale between the individual optimum points. If the Gasoline has much higher market value than LCO, the optimum operation will be closer to the MGY point, and in the case where LCO has much higher market value than Gasoline, the optimum operation will be closer to the maximum LCO point.

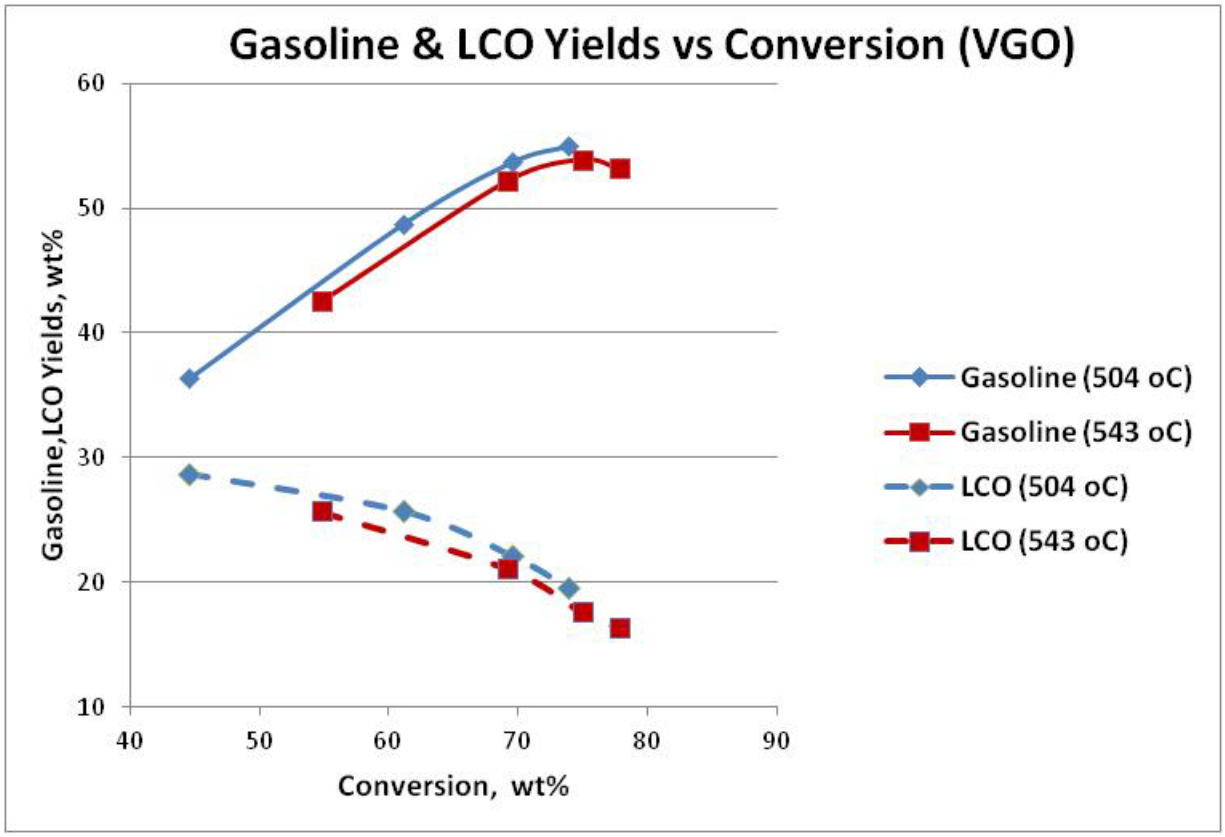

Figure 4 Gasoline and LCO Yields vs. Conversion

5. Summary

The work presented in this paper emphasized using models for experimental data interpretation. Although the ACE apparatus is a well recognized petroleum industry-wide workhorse for laboratory catalyst and feed evaluations, it has some limitations with the range of testing conditions that can be practically utilized.

The experimental data from the ACE testing frequently do not cover the conversion range that is wide enough for finding optimum performance points. Extrapolations of testing results have obvious limitations related to the lack of understanding of complex catalyst-feed interactions that hinders the prediction of the type and shape of the curve representing the particular property outside of the experimental domain. In addition, experimental results always carry an error associated with the accuracy of a particular test or procedure, which makes the interpretation even harder. On the other hand, statistical models and correlations used in this work allow not only deciphering the fundamental relations and influences of typical feed and/or catalyst properties on FCC cracking selectivity but also filtering out errors and experimental biases.

While statistical models were successfully used in this work for experimental data extrapolation, they also have limitations on how far from the experimental domain the prediction is still valid. Another class of models mentioned but nor used in this work, based on the fundamentals of transport phenomena, reaction engineering, and thermodynamics, can be used to model a much broader range of conditions, but they too have their limitations related to the model complexity mostly due to the enormous number of

different chemical compounds involved and the lack of reliable information about those compounds' physical properties and reactions rates in scientific literature.

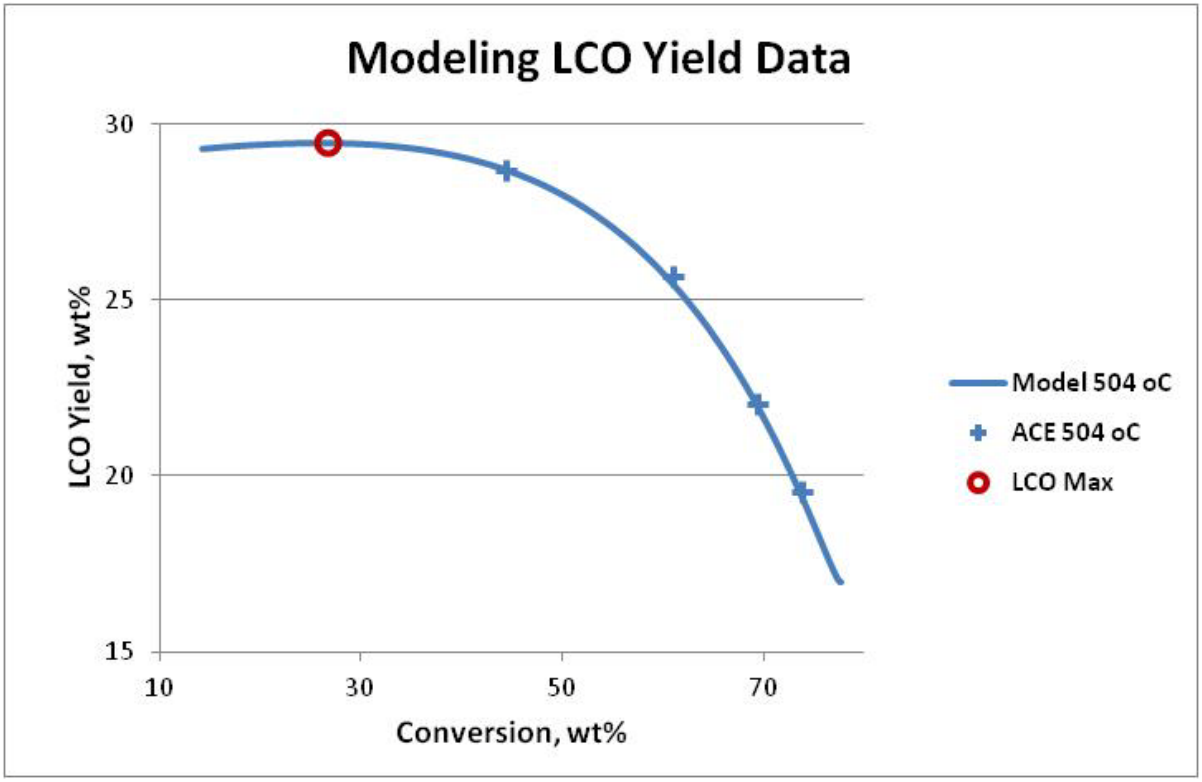

Figure 5. Application of statistical model for LCO Yield data extrapolation

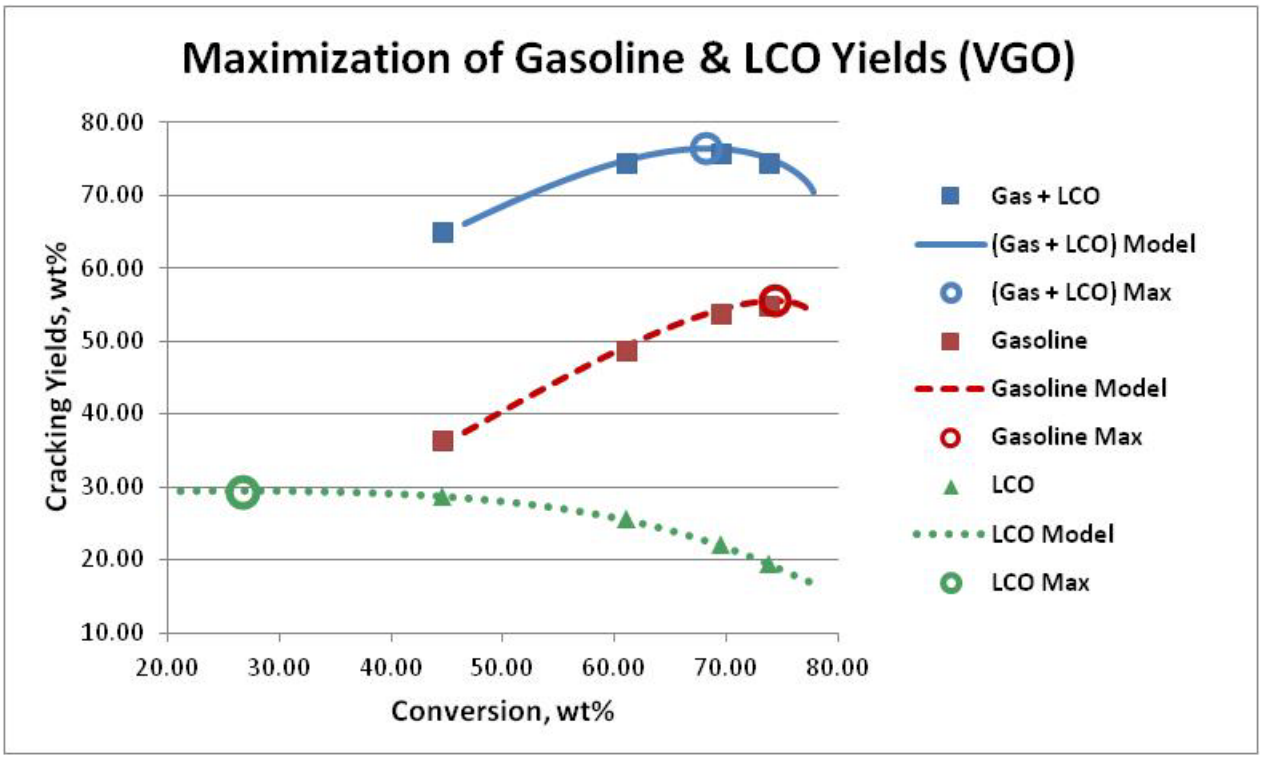

Figure 6. Gasoline and LCO maximization

6. References

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