Optimization of Refining Alkylation Process Unit using Response Surface Methods

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Abstract

This paper illustrates a methodology to optimize the operations of an alkylation unit based on response surface methods. Trial based process optimization requires the unit to be operated across a wide range of conditions. This approach tends to be opposed by refinery operations as it can disrupt the normal operations of a process unit. Using the methods presented in this paper, the general direction of process improvement is first identified using a first order profit response surface built from available operating data. The performance of the unit is then evaluated at the refinery by making systematic changes to the key factors in the projected direction of process improvement. The operating results are then used to build a localized second order profit response surface to generate a revised set of optimum targets. Multiple linear regression models are used to predict alkylate yield, alkylate octane and Iso-stripper or De-Isobutanizer reboiler duty as a function of key process variables. These models are then used to generate a profit response surface for selection of an optimum target region for step testing at the refinery prior to implementation of the unit targets.

1. Introduction

An alkylation unit takes a feed stream with a high olefin content, typically originating from a fluid catalytic cracking (FCC) unit, and adds isobutane (IC4) which reacts with the olefins to produce a high octane alkylate product. Either hydrofluoric or sulfuric acid is used as a catalyst for the alkylation reaction. In the operation of an alkylation unit, a higher IC4 to olefin ratio (I/O) typically results in higher octane and yield but at the expense of increased energy use. The increased energy use arises from having to achieve a higher iC4 purity in the distillation section of the alkylation unit. Acid strength is also a key process variable that needs to be maintained within a range to ensure the octane number target is met and also to prevent an "acid runaway" reaction that can occur when the acid strength is too low. The optimum targets for these factors depend on the market value of the alkylate product, the octane gasoline blending value, and energy costs. This study uses response surface methods to optimize the targets for I/O ratio and acid strength as these two factors are significant drivers in maximizing the unit profitability.

Figure 1 is a typical process flow diagram of a hydrofluoric (HF) acid alkylation unit. The fresh olefin feed is combined with isobutane (IC4) before entering the reactor where the olefins react with IC4 in the presence of hydrofluoric acid catalyst. The reaction forms higher molecular weight iso-paraffins with an associated increase in the octane number. The mixture of the higher molecular weight iso-paraffins and unreacted IC4 go into an iso-stripper unit where it is separated into a rich IC4 stream and the alkylate product. The rich IC4 stream goes into a depropanizer where propane is removed and the IC4 is recycled back to the reactor [1].

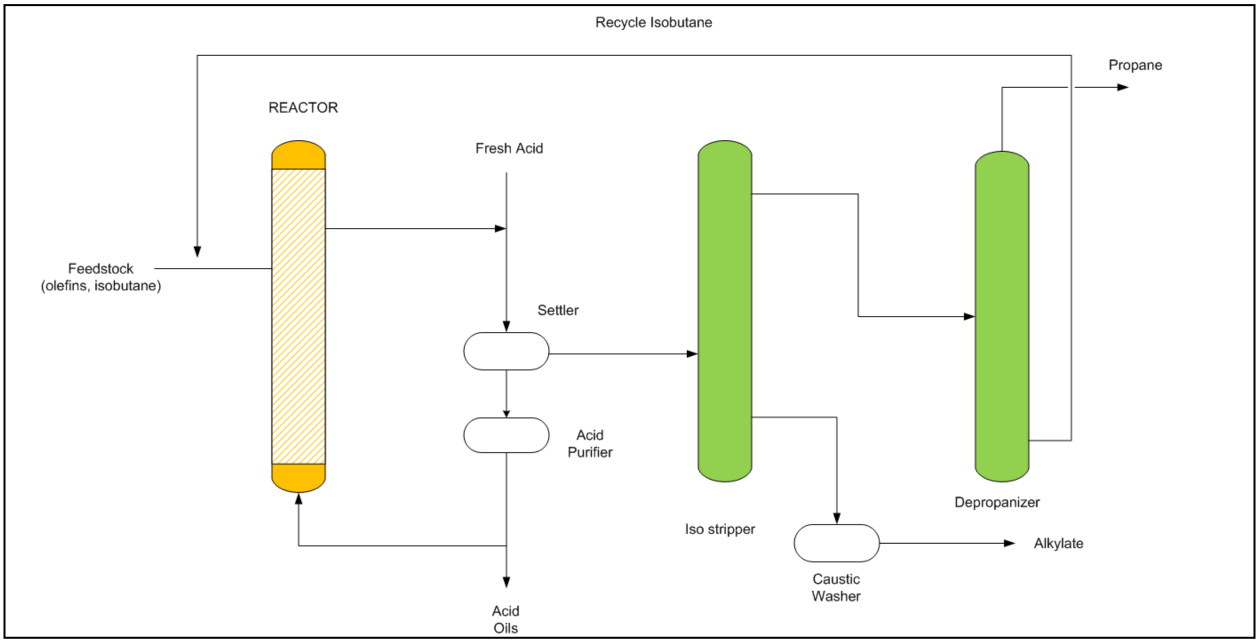

Figure 1: Aklylation Unit Schematic

This study uses multiple linear regression models constructed using actual operating data to predict alkylate yield, alkylate octane, and iso-stripper reboiler duty as a function of key process variables which include I/O ratio, acid strength, and reactor temperature. The multiple regression models are then used to construct 3D response surfaces represented as contour maps. A profit response surface is then generated based on these models to map the alkylation unit profit as a function of I/O and acid strength. The profit response surface identifies an optimum target operating region for refinery step testing.

The following summarizes the methodology used in the study: 1) build multiple linear regression models for alkylate yield, alkylate octane, and iso-stripper reboiler duty as a function of key process variables, 2) use models to generate response surfaces to visually examine relationships of the responses with key factors, 3) generate a profit response surface given the current market value of alkylate, energy and octane based on multiple regression models for the three responses, and 4) identify an optimum target operating region for field testing at the refinery prior to implementation of the unit targets. The study followed these steps as part of a screening analysis which was based on 2.5 years of operating data. A more detailed assessment following these steps was then conducted using six months of recent operating data.

A detailed description of the construction of the multiple linear regression models is provided below, followed by the economic optimization analysis, and the study conclusions.

2. *Multiple Regression Analysis*

Before construction of the multiple regression models [2], an exploratory analysis was conducted to examine the distributions of the key process variables as well as the relationship among these variables. A data set that was representative of normal unit operations was also selected at this step. Table 1 is a summary providing key statistics including the average, standard deviation, and selected percentile point values for each of the process variables considered. The percentile point values highlight the range and variability associated with each variable. Alkylate yield, alkylate octane (RON), and iso-stripper reboiler duty ratio are also shown as these three process responses are needed to construct the profit function. Alkylate yield was defined as the total alkylate production volume divided by the olefin feed volume. The iso-stripper reboiler duty ratio was defined as the iso-stripper reboiler duty in MMBTU/hr divided by the olefin feed in MBPD. The SAS procedure PROC MEANS [3] was used to generate the statistics summary.

Variable	Mean	Std Dev	1st Pctl	10th Pctl	25th Pctl	75th Pctl	90th Pctl	99th Pctl
yield	1.8	0.2	1.3	1.5	1.7	2.0	2.0	2.3
RON	92.6	0.6	91.3	91.9	92.1	92.9	93.3	94.3
IO	9.9	1.2	7.2	8.4	9.1	10.5	11.3	13.9
IC4_purity	78.1	3.1	71.3	73.9	76.0	80.4	82.3	85.2
Olefin_feed	5.9	0.8	4.0	5.0	5.4	6.4	7.0	7.6
feed_butylene	48.3	4.3	36.2	43.0	45.8	50.8	53.8	57.3
acid_strength	90.8	1.9	86.5	88.4	89.5	92.0	93.2	96.4
duty_ratio	11.0	2.3	7.7	8.6	9.4	12.4	13.9	18.4
BTU_content	823.5	89.5	674.9	735.8	760.3	880.2	951.9	1073.3
effluent_temp	94.6	5.7	80.8	86.8	90.7	98.9	101.4	105.8

Table 1: Statistics Summary

Figure 2 is a scatter plot matrix illustrating the relationships between pairs of variables as well as the distribution of each variable. Strong linear relationships between alkylate yield and both I/O ratio and acid strength are evident. The research octane number (RON) was found to be highly correlated with reactor temperature, feed butylenes, and the IC4 recycle purity. As expected, iso-stripper reboiler duty ratio is highly correlated with I/O ratio. The SAS procedure PROC SGSCATTER [3] was used to generate the scatter plot matrix.

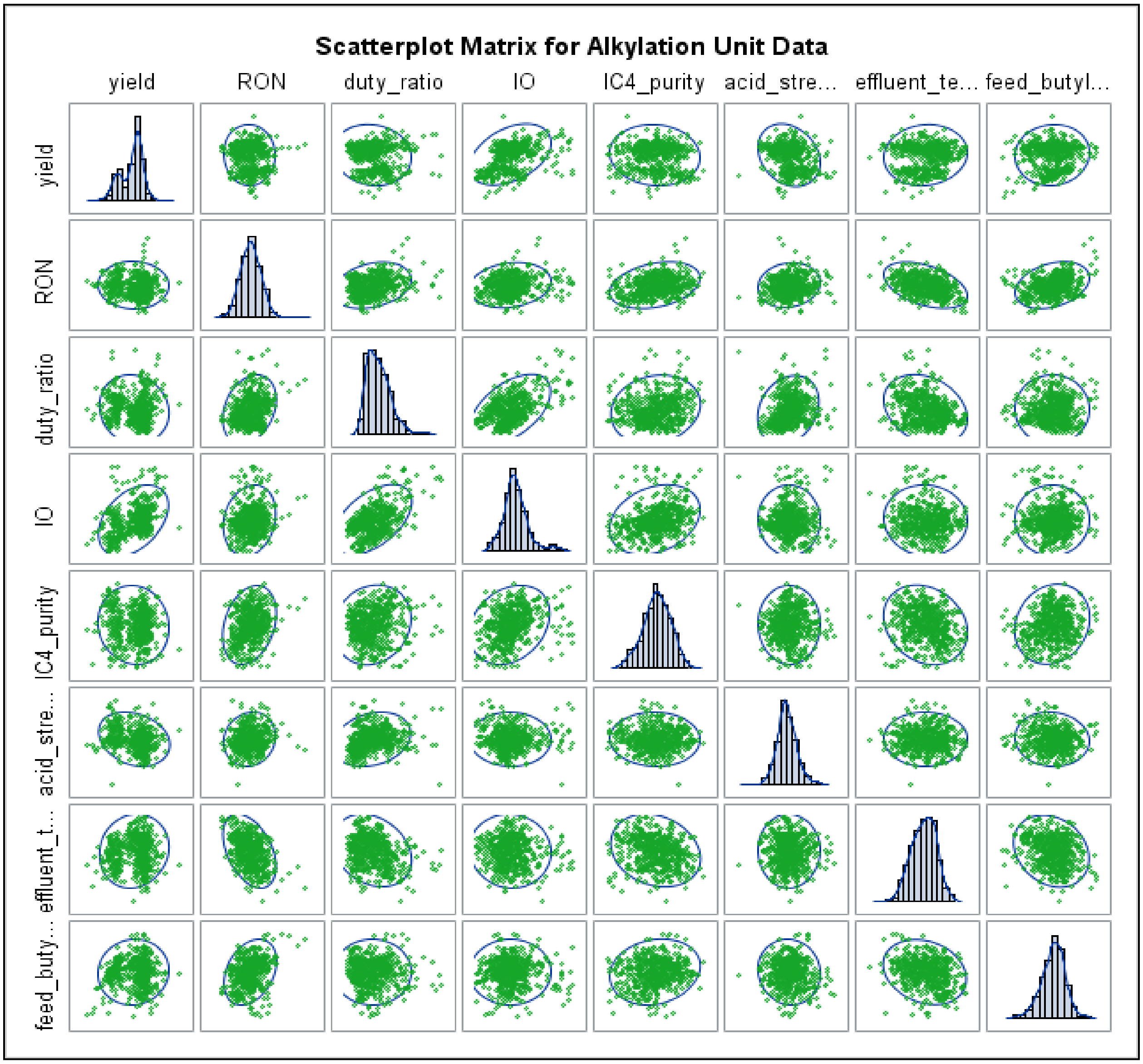

Figure 2: Scatter Plot Matrix

Before building the multiple regression models for each response, process inputs were transformed into dimensionless quantities with values ranging from -1 to +1 and a mean of 0.

Dimensionless quantities, also known as coded values in response surface methodology [4,5], allow for quick assessment of the contribution of the different inputs for a given response. The computation of the coded values is given below:

Coded value=(Raw value-M)/S
where: M = average of Maximum and Minimum values
S = (Maximum – Minimum values)/2

Multiple linear regression models were constructed for each of the responses using the following set of predictors: I/O ratio, IC4 recycle purity, acid strength, feed butylenes content, and reactor temperature. First order models were built based on 2.5 years of daily operating data to assess the general direction of process improvement. In addition to the factors mentioned above, the fuel gas BTU content was considered when modeling the iso-stripper reboiler duty ratio to account for the variability attributed to this factor. The SAS procedure PROC GLMSELECT [3] was used to build the first order models. Figures 2-4 illustrate the progression of the standardized regression coefficient values and the associated significance level (p value) at each step of the stepwise selection process. These charts illustrate the relative importance of each variable in predicting each response. Standardized regression coefficients are calculated using standardized values for the response and the predictors, which have a mean of 0 and a standard deviation of 1. By standardizing these values, the same scale is used for each variable when computing the regression coefficients and this provides an assessment of the relative contribution of each predictor variable.

Figure 3 shows that I/O ratio is the most influential variable in predicting alkylate yield as it has the largest magnitude of the standardized regression coefficients. The sign of the coefficient indicates the direction of the relationship so an increase in I/O ratio is associated with an increase in alkylate yield. IC4 recycle purity was also found to be statistically significant. However, in this case the negative sign of the coefficient was contrary to expectation and this behavior is probably a result of cross correlation between I/O ratio and IC4 purity. The I/O ratio increases with IC4 recycle purity at a constant recycle flow rate due to the higher concentration of IC4 in the recycle stream. Since I/O captures most of the impact on yield, acid strength was chosen as the second variable to optimize as this factor appears to have a negative impact on yield at higher acid strengths. Figure 4 shows that reactor temperature is the most influential variable in predicting octane number with higher octane values associated with lower reactor temperatures. Since reactor temperature is mainly driven by ambient temperature, this variable was not the focus of the analysis as this variable is already being managed at the refinery within the reactor limits. Figure 5 shows that I/O ratio was the most significant variable to predict the iso-stripper reboiler duty.

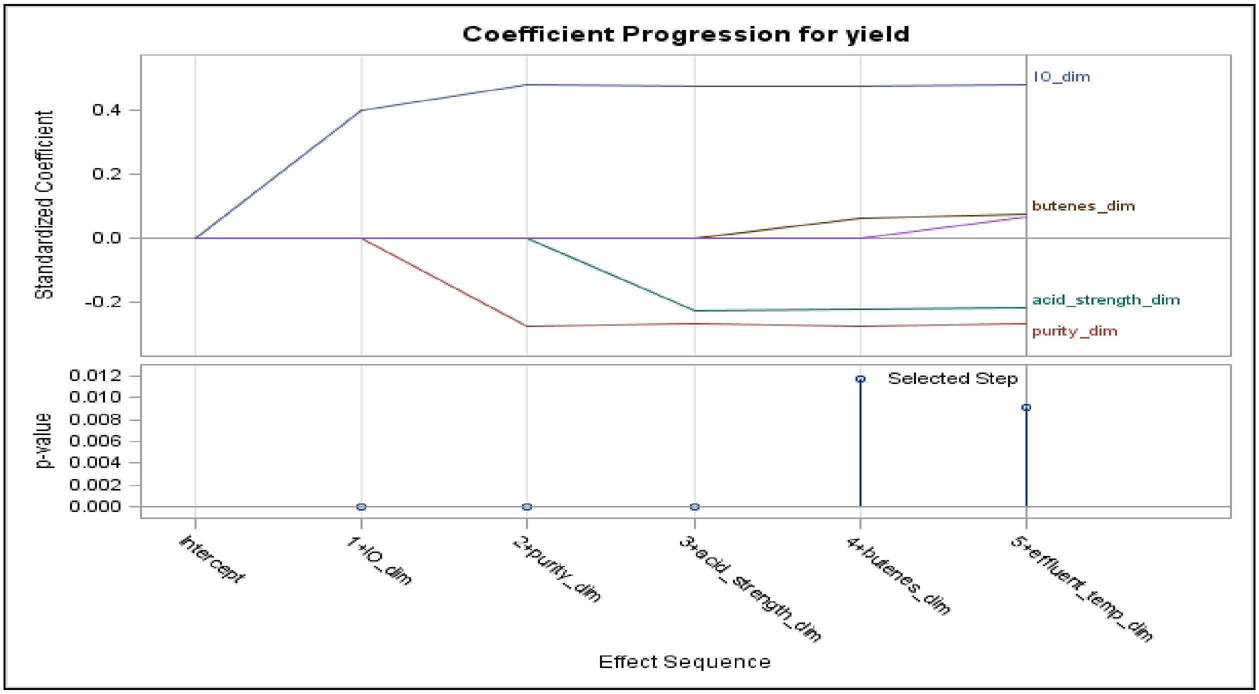

Figure 3: Coefficient Progression for Yield

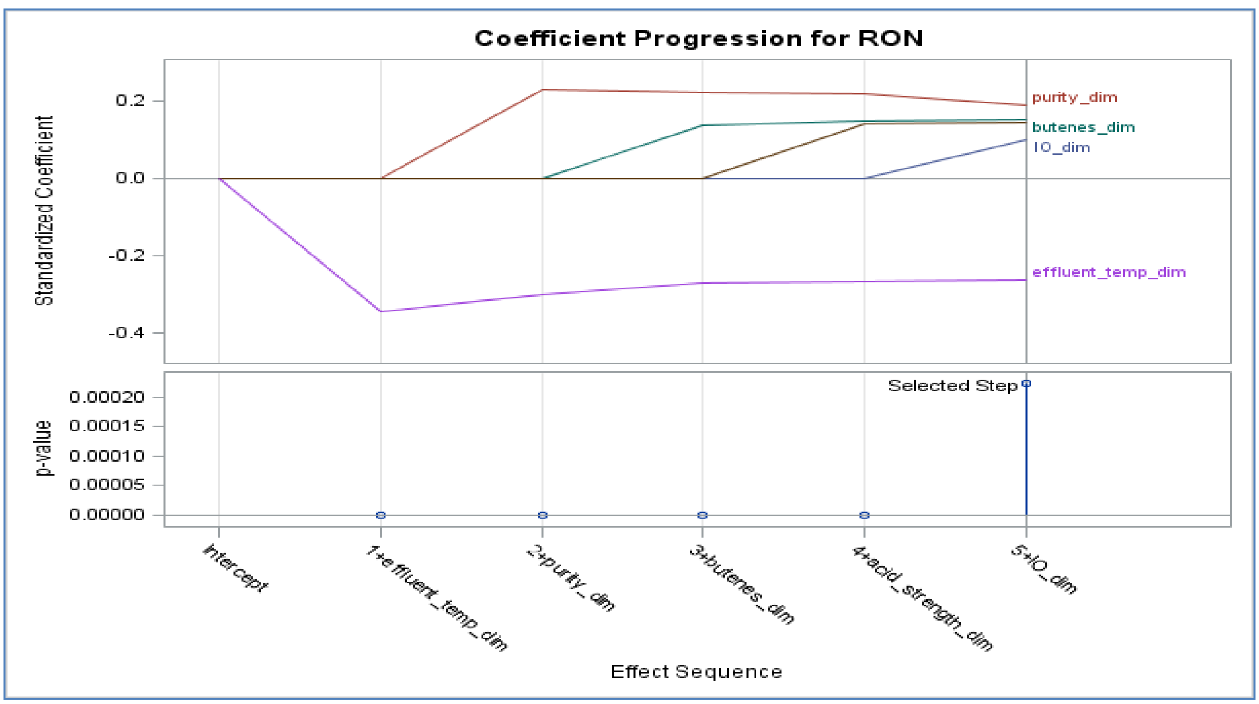

Figure 4: Coefficient Progression for RON

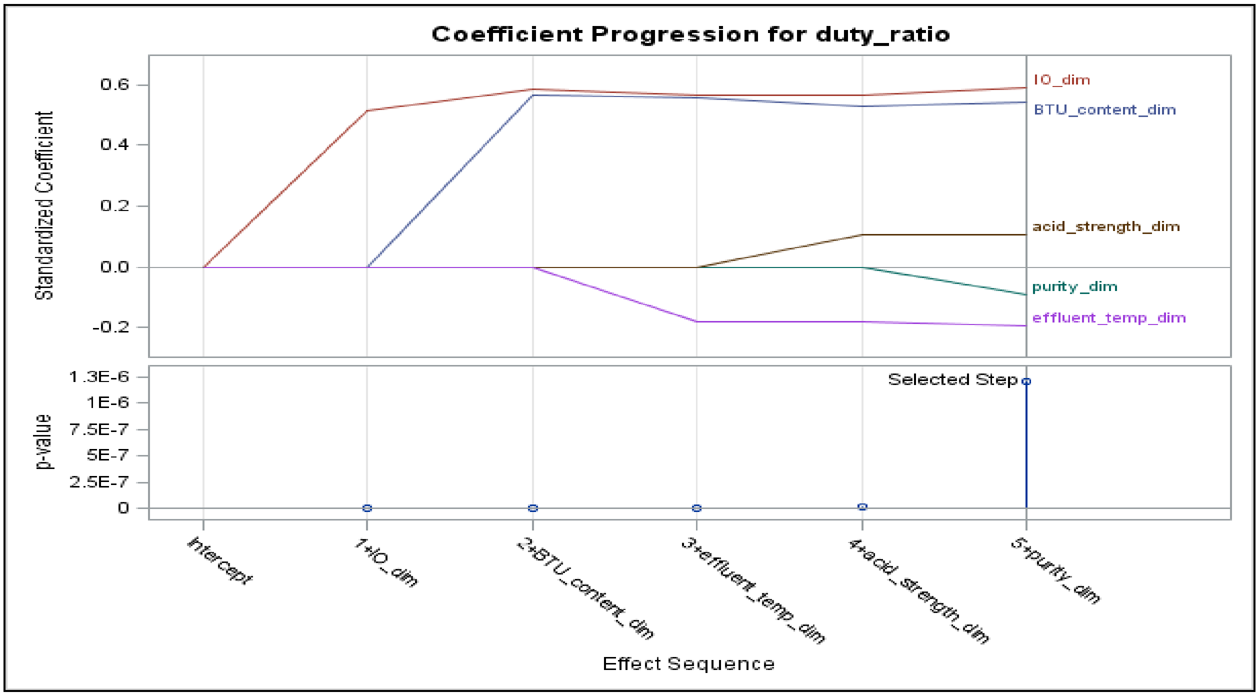

Figure 5: Coefficient Progression for Reboiler Duty ratio

3. *Economic Optimization Analysis*

Screening Analysis

First order multiple linear regression models were built for alkylate yield, octane number, and iso-stripper reboiler duty ratio. These models were then used to generate a profit response surface to identify the general direction of process improvement. Prior to constructing the profit response surface, contour maps of the three responses were generated to ensure the models properly represented the relationships between the responses and the inputs. To generate the contour maps, the multiple regression models were evaluated at the average values for all of the factors with the exception of the I/O ratio and the acid strength which were the two variables to be optimized. Figures 6-8 show the alkylate yield, octane number, and the iso-stripper reboiler duty response surfaces. Figure 5 shows that alkylate yield is maximized at the higher I/O ratios and lower acid strengths. Figure 7 shows RON is maximized at the higher I/O ratios and higher acid strengths. Figure 8 shows that iso-stripper reboiler duty ratio increases with I/O ratio as expected. As will be demonstrated below, the test region shown represents the predicted region of maximum profitability. The SAS procedure PROC GCONTOUR was used to generate the contour maps of the responses [3].

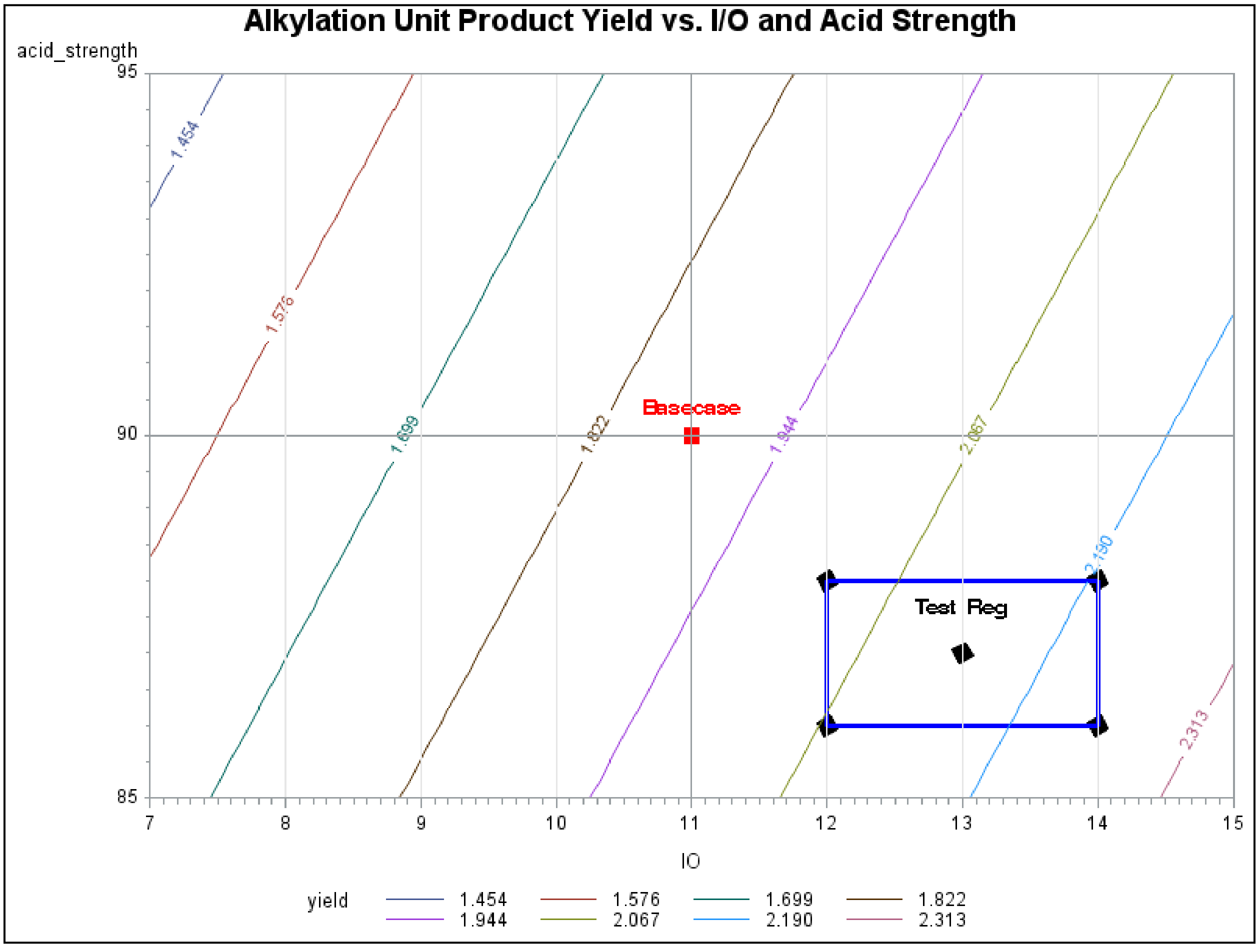

Figure 6: Yield vs. I/O and Acid Strength Contour Map

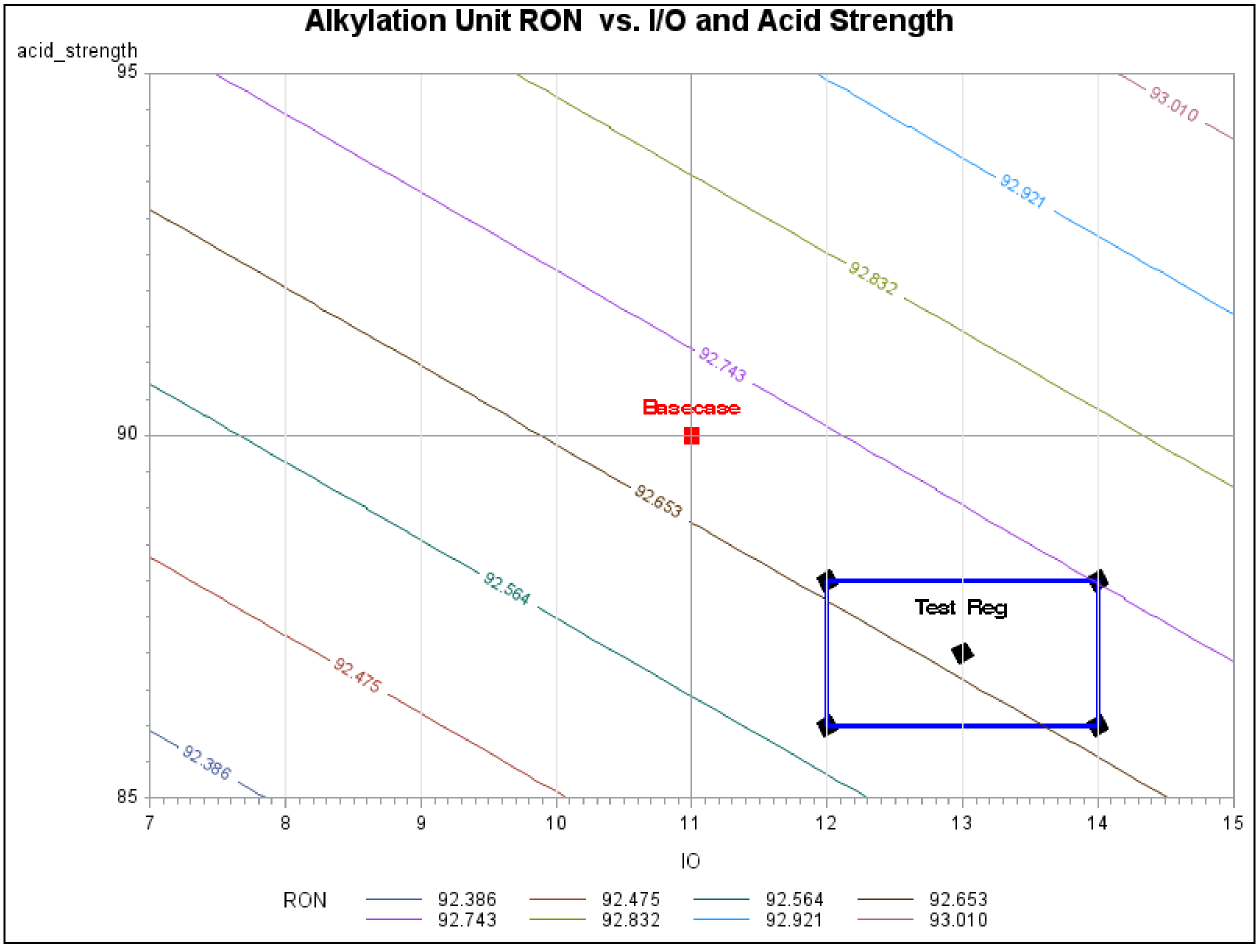

Figure 7: Octane Number vs. I/O and Acid Strength Contour Map

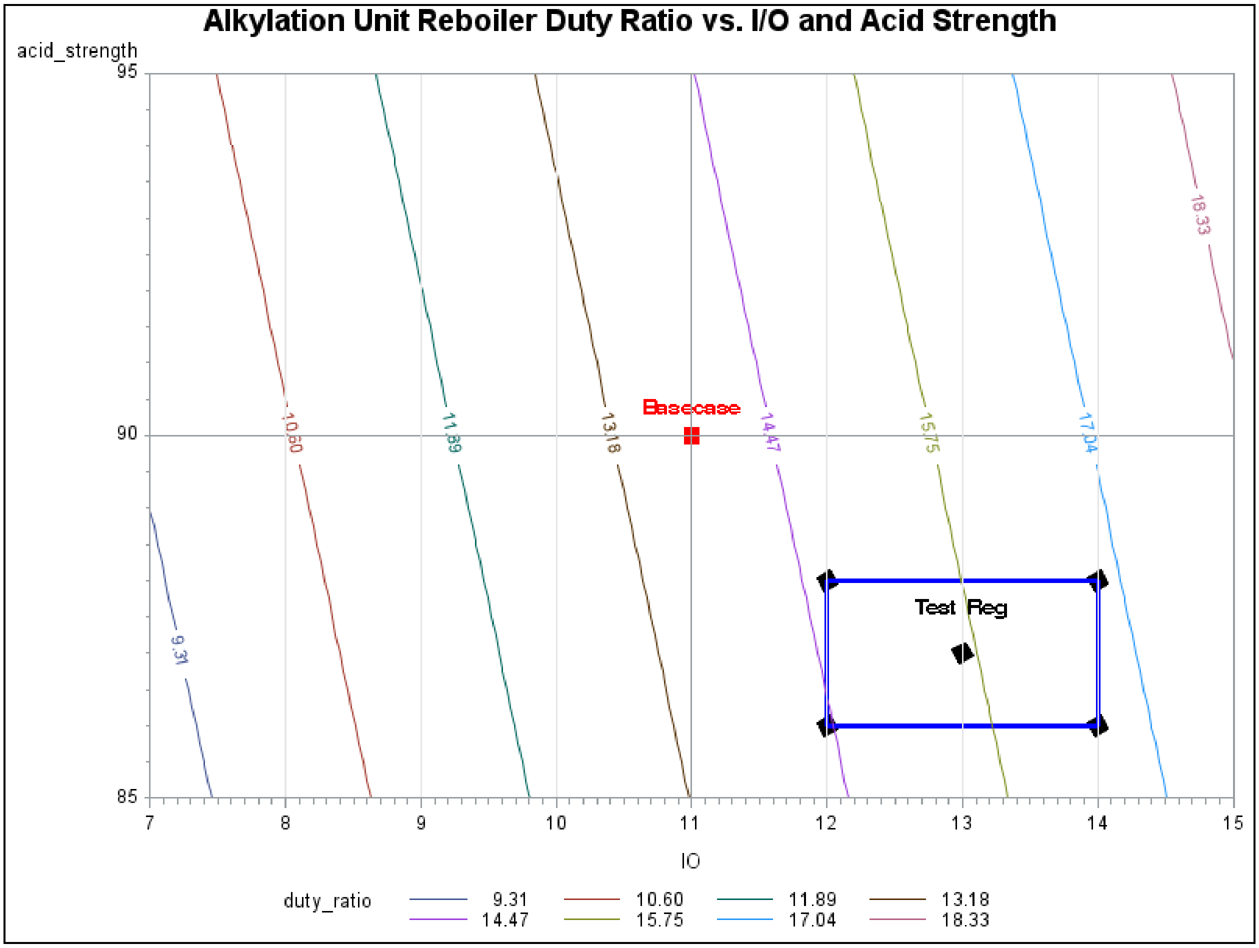

Figure 8: Reboiler Duty Ratio vs. I/O and Acid Strength Contour Map

The predicted values for yield, octane, and iso-stripper reboiler duty ratio were used to compute the profit response surface expressed as the incremental profit vs. a reference case. The reference case was defined at an I/O ratio of 11 and an acid strength of 90%. These values represent the middle of the operating range for the data considered. The calculated incremental profit was expressed in dollars per barrel of olefin feed to normalize out the effect of olefin feed rate. To compute the yield and octane benefits, an incremental margin of alkylate versus IC4 of $48/bbl was assumed along with an octane gasoline blend value of $2 per octane barrel. The energy cost per barrel of olefin feed basis was calculated assuming a $5/MMBTU fuel gas price.

Figure 9 shows the incremental profit response surface. The highest values for incremental profit are observed at the higher I/O ratios and lower acid strengths. The test region is also shown which covers I/O ratios ranging from 12-14 and acid strengths from 86 to 88%.

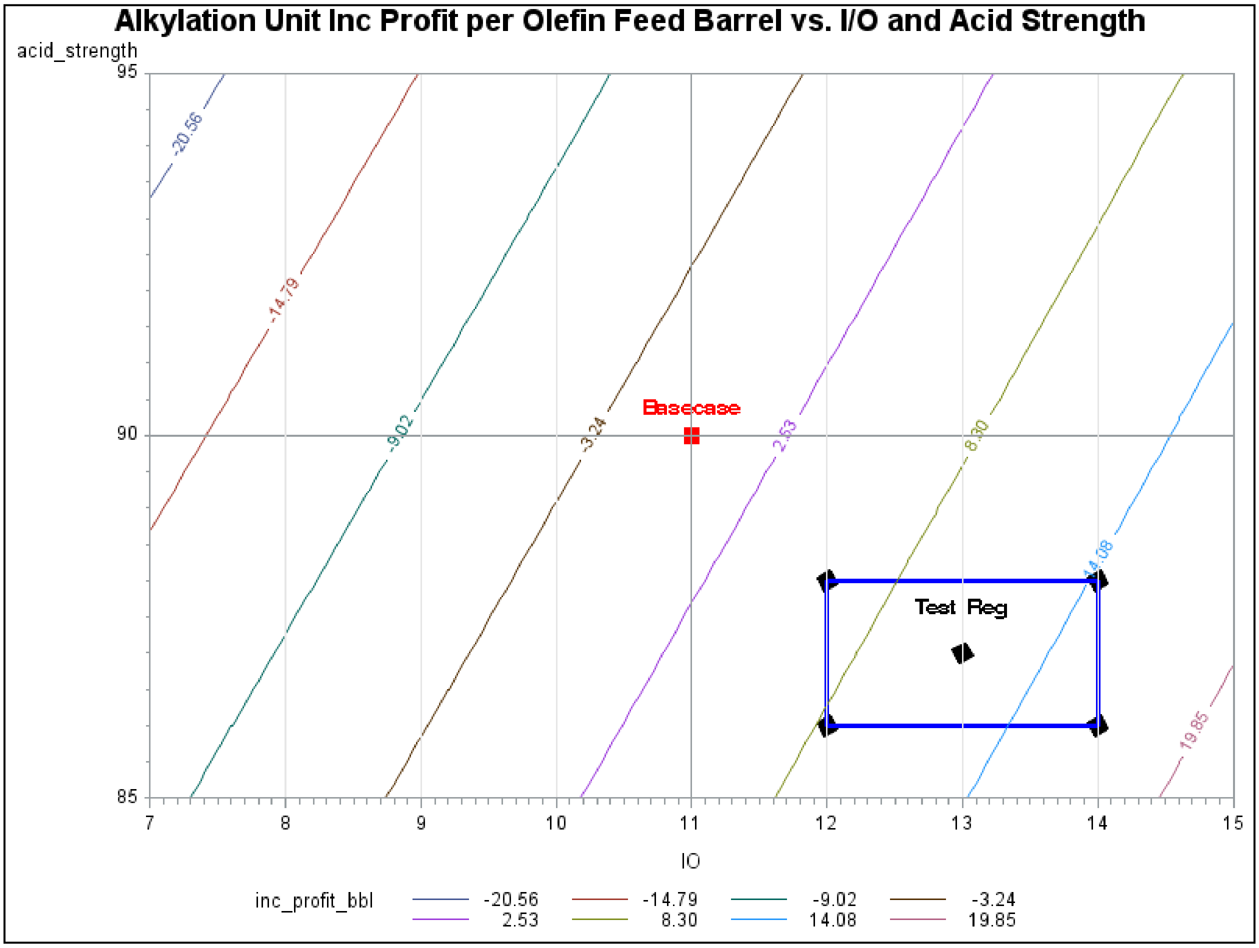

Figure 9: Incremental Profit per Barrel vs. I/O and Acid Strength Contour Map

Detailed Assessment

Based on the results of the screening analysis, a set of trials were recommended to evaluate the performance of the unit at the higher I/O ratios and lower acid strengths. A central composite design (CCD) scheme was considered as a starting point which uses center, corner and axial runs within the experimental region [4,5]. However, to minimize the impact on unit operations, it was decided to limit testing to adjusting the I/O ratio as this was the most significant factor impacting the unit economics. Due to reactor temperature limit constraints in the summer months, initial testing was limited to I/O ratios ranging between 8 and 11.

The screening analysis was based on 2.5 years of operating data which was heavily weighted to data without the selective hydro-isomerization unit (SHU) running. On the other hand, the detailed assessment used a more balanced data set consisting of 3 months of operations prior to the SHU startup and 3 months after the SHU startup. To evaluate the benefits associated with running the SHU, both data prior to and post to the startup of the SHU was selected. The SHU pre-conditions the alkylation unit feed by converting 1-butene and 1-3 butadiene to 2-butene which has a higher octane number when reacted to alkylate products. The 1-3 butadiene component also increases acid consumption so acid consumption is reduced by converting the 1-3 butadiene to 2-butene.

A binary 0-1 variable, also known as indicator variable, was used to identify when the SHU was running. Figures 10-13 show contour plots of yield, RON, duty ratio, and incremental profit per barrel as a function of I/O ratio and acid strength based on the multiple linear regression models built using the 6 months of operating data. The SAS procedure PROC RSREG [3] was used to build these models which were second order models that included quadratic and interaction terms in addition to the first order terms.

Figure 10 shows that alkylate yield is maximized at the higher I/O ratios and acid strengths. Figure 11 shows that RON is maximized at the higher I/O ratios and in the 90-92% acid strength range. Figure 12 shows increasing reboiler duty with I/O ratios as would be expected. As Figure 13 shows, the economic optimum occurs at the higher I/O ratios and acid strengths mostly resulting from the higher predicted yields. The results of the detailed assessment which predicted improved performance at the higher acid strengths are not surprising as SHU treated alkylation unit feed can tolerate much higher acid strengths than untreated feed. In constrast, the screening analysis predicted improved performance at somewhat lower acid strengths (86-88%) but most of the data used for the screening analysis was more heavily weighted towards operations without the SHU.

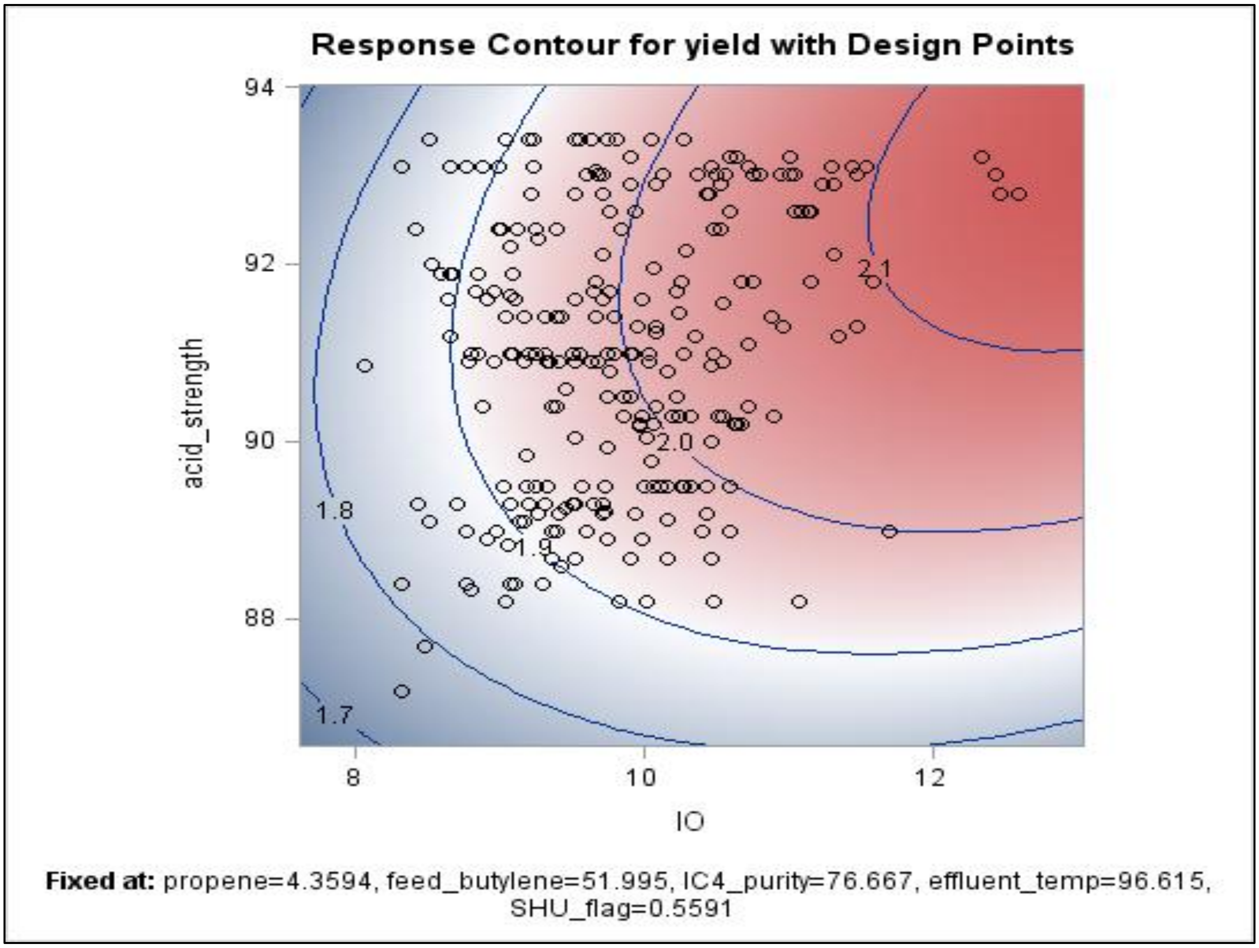

Figure 10: Yield vs. I/O and Acid Strength Contour Map

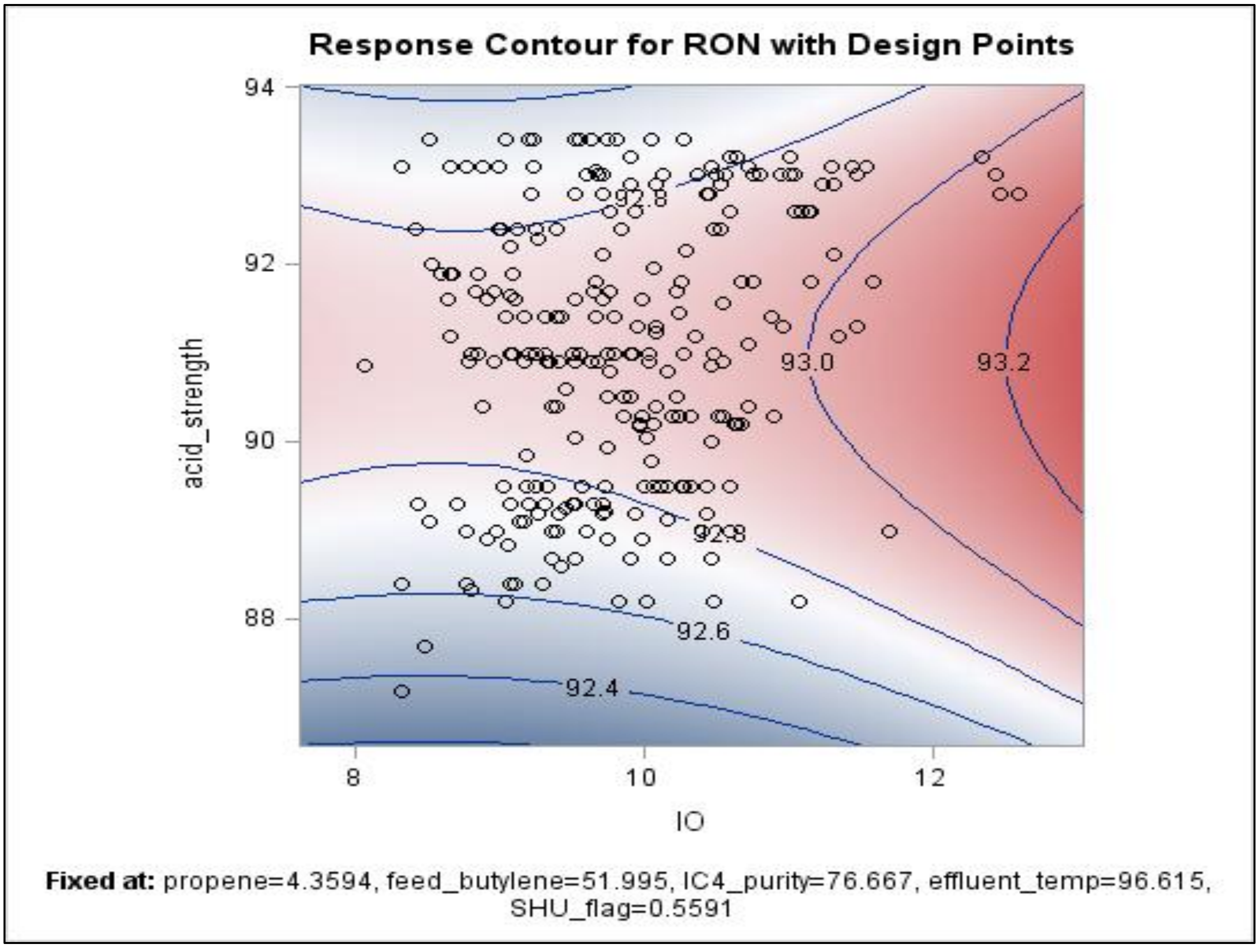

Figure 11: RON per Barrel vs. I/O and Acid Strength Contour Map

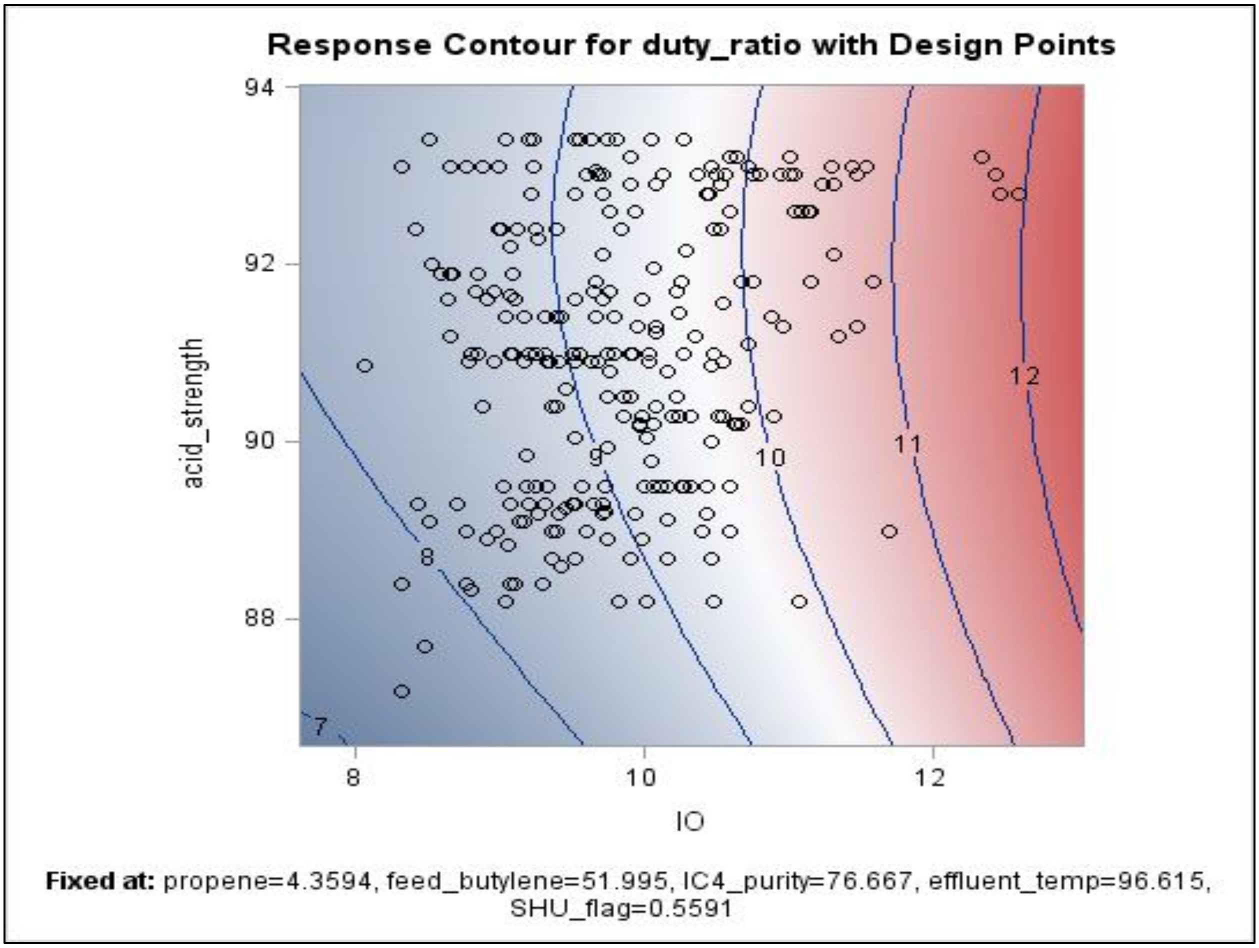

Figure 12: Reboiler Duty Ratio vs. I/O and Acid Strength Contour Map

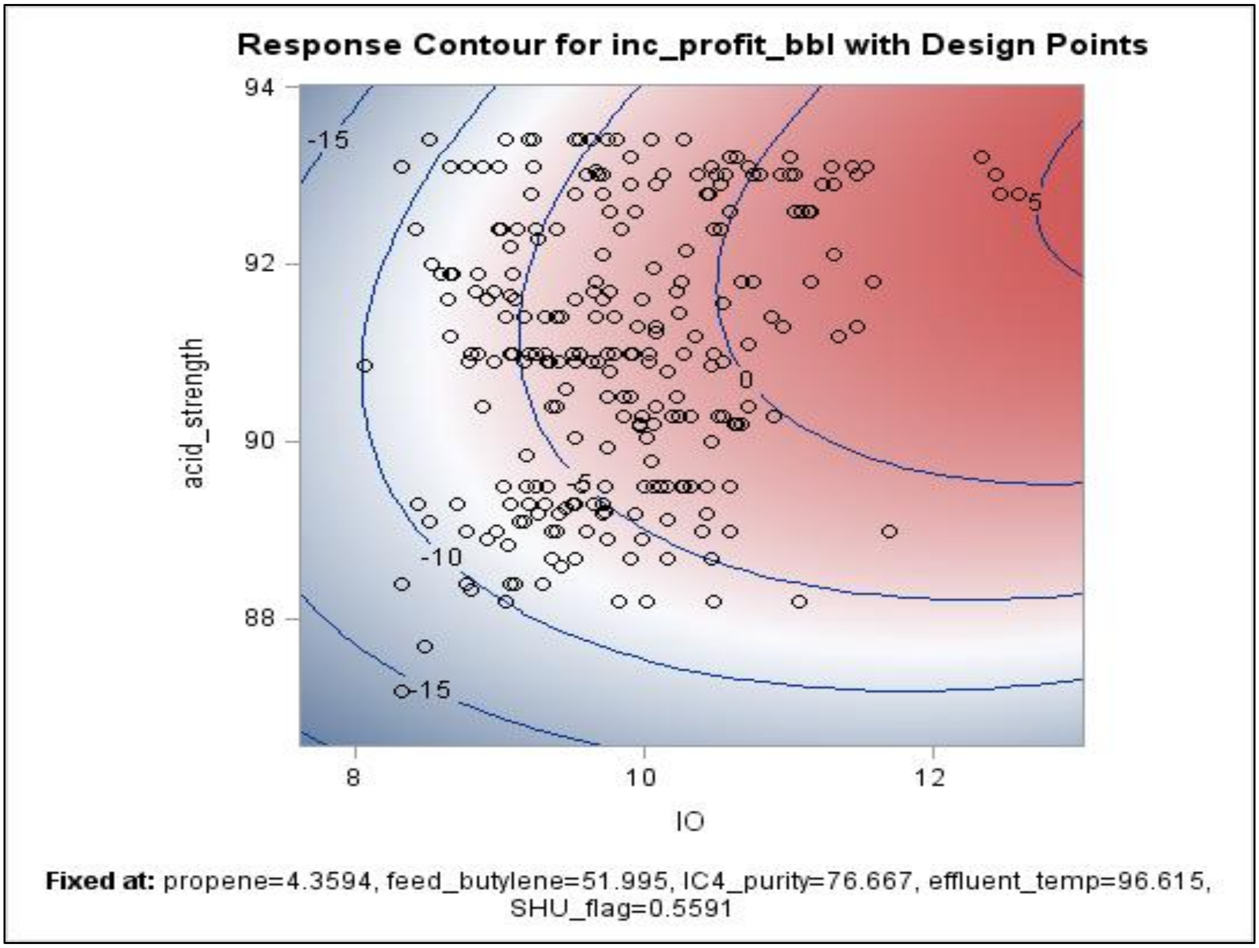

Figure 13: Incremental Profit per Barrel vs. I/O and Acid Strength Contour Map

As mentioned previously, the reactor was temperature limited during the summer months. The two temperature limits that constrain the operations in the summer are: 1) a 100^0F limit to prevent a decline in alkylate RON and 2) a 110 ^{0}F limit to minimize tar formation which can lead to a reduction in acid strength. The decline in the RON at the higher reactor temperatures can be seen in Figure 14 which shows a contour map of the RON as a function of I/O ratio and reactor temperature. The decline in RON appears to be more significant at the lower I/O ratios. Figure 15 also shows the significant octane benefits being realized by pre-conditioning the alkylation unit feed with the SHU.

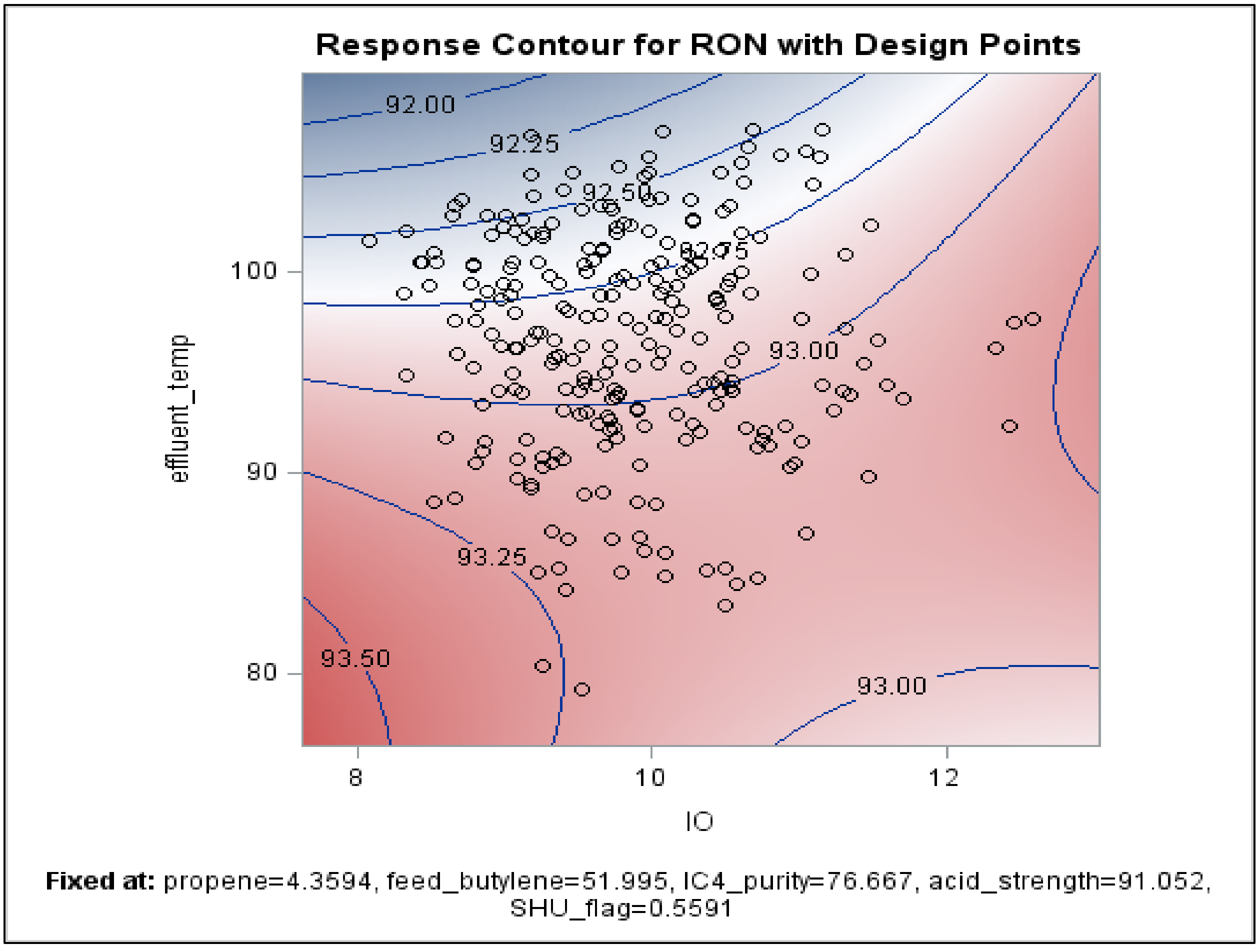

Figure 14: RON vs. I/O and Reactor Temperature Contour Map

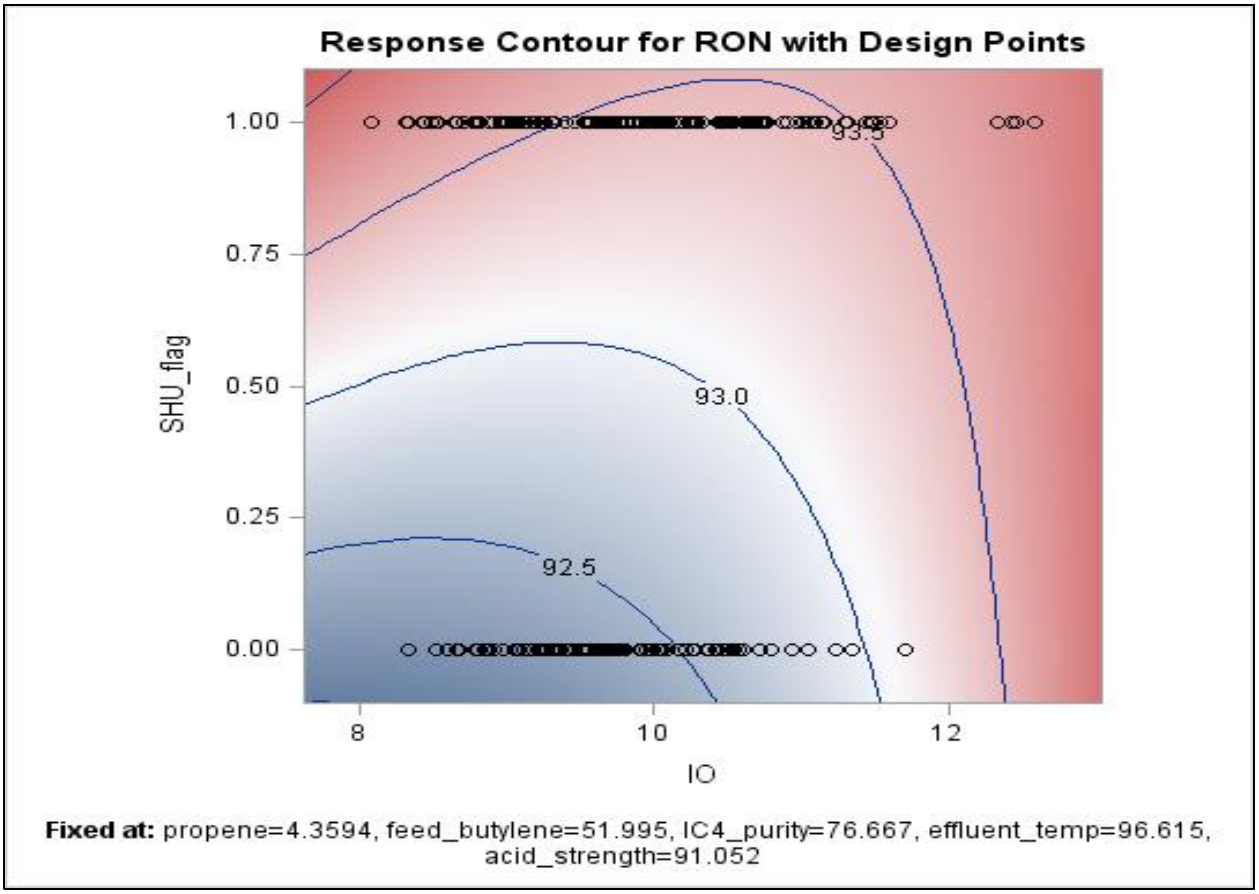

Figure 15: RON vs. I/O and SHU Unit Operation Flag Contour Map

Future plans call for running at higher I/O ratios once ambient temperature drops to validate the benefits predicted in this analysis. Based on the estimated yield and octane benefits of running at higher I/O ratios and assuming future field testing confirms these results, an operating strategy is being considered which consists of increasing the I/O ratio up to a maximum of 12 when feasible.

Figure 16 is a contour map of reactor temperature as a function of I/O ratio and reactor cooling water temperature for one year of operation. This contour map is based on a linear regression model that predicts reactor temperature as a function of I/O ratio, cooling water basin temperature, and olefin feed rate. Note the significant impact of cooling water basin temperature on reactor temperature. When cooling water basin temperature exceeds 90 ^{0}F, the reactor temperature exceeds the 100 ^{0}F limit set to prevent a decline in alkylate octane. A significant number of the operating data points are below the reactor temperature limit of 100 ^{0}F and an I/O ratio below 12 which highlights potential opportunities to increase yield and octane.

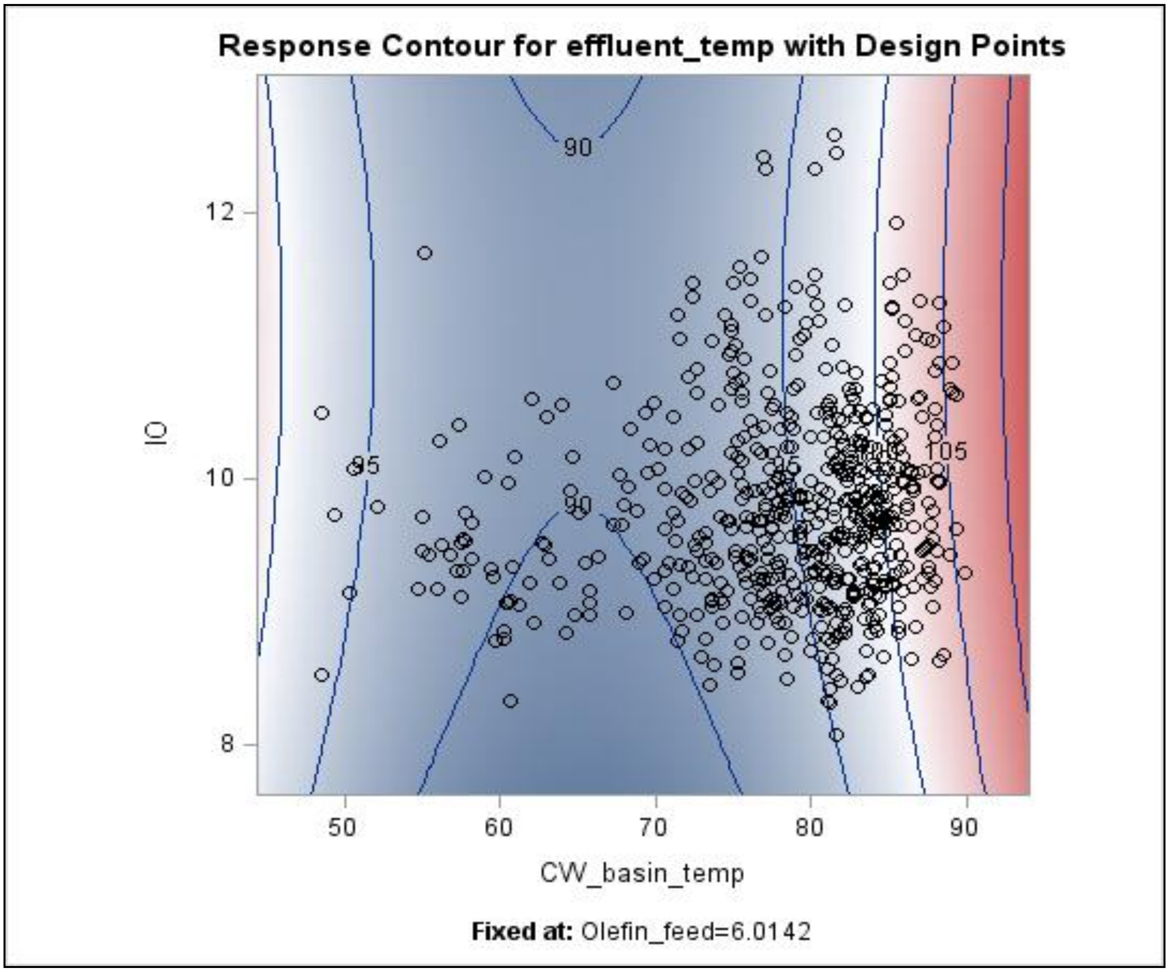

Figure 16: Reactor Temperature vs. I/O and Cooling Water Temperature Contour Map

4. Conclusions

This paper illustrates the optimization of a refining alkylation unit using response surface methods. Multiple linear regression analysis was used to generate response surfaces for alkylate yield, octane number, and iso-stripper reboiler duty ratio as a function of key process variables including I/O ratio, acid strength and reactor temperature. A profit response surface was then constructed using the multiple regression models of the three responses. The analysis estimated an optimum I/O ratio target of 12 and optimum acid strength in the range of 92-94%. The path forward is to validate the results of the analysis by running at higher I/O ratios during the winter months when the reactor is not temperature limited. The methodology presented in this paper can be used to optimize other refining and petrochemical units where the process unit profit function can be represented via multiple linear regression models.

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