OPTIMIZATION AND ANALYSIS OF AN ALKYLATION PROCESS USING GEOMETRIC PROGRAMMING

by

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ABSTRACT

This thesis compares geometric programming (GP) as a viable alternative to simplify the optimal design for a chemical process, alkylation, which allows the motor octane number of isoparaffinic gasolines to increase. The alkylation process is discussed and the critical variables (independents and dependents) presented.

The original model presented by Sauer, et al., [10] is modified and solved using geometric programming techniques, reducing the complexity of the problem. An heuristic approach to solve the original problem is presented and comparisons between this solution and the GP solution are interpreted with regard to accuracy and significance. The contribution this paper has made in the area of optimization of chemical processes is presented and areas for future research are discussed.

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DEDICATION

To my Dad, whose inspiration has always been the wind that fills the sails of my dreams.

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INTRODUCTION

Practical ways are still needed for optimizing the design of chemical processes, with allowances for uncertain specifications and future changes in economic parameters. Some practical approaches for solving the problem of optimum design have been proposed in the literature (see for example Wen & Chang [1]; Saletan [2]; Berryman & Himmelblan [3]; Powers & Mayer [4]). Many of these methods appear promising, but none has yet been applied successfully to an entire process design. These methods are based on statistical descriptions of the parameter uncertainties, usually in terms of probability distribution functions. The main drawback is that all require the use of computer time which implies an additional cost. A more recent method has been proposed by Malik and Hughes [5] which consists of direct analysis of the stochastic multistage decision problem. Again, this method requires the analysis to be performed with the aid of a computer model.

The purpose of this thesis is to simplify the optimal design for a chemical process, alkylation, by using geometric programming as an optimization technique to solve the problem.

Geometric programming (GP) is a mathematical programming technique used to optimize nonlinear problems. This is done with the use of linear equations using the dual, which will obviously make the calculations easier. The final form of the objective function, which represents the optimization design problem, will be simpler and easier to analyse. This represents the main advantage of GP over the methods proposed in the literature: a simplified form of the problem to provide the design engineer with a feeling of the important variables in the process.

Chapter 1

ALKYLATION

In petroleum refining terminology, the term "alkylation" is used to describe the reaction of low molecular weight olefins with an isoparaffin to form higher molecular weight isoparaffins [6]. The need for high-octane aviation fuels during World War II acted as a stimulus to the development of the alkylation process for production of high octane number isoparaffinic gasolines.

Although alkylation can take place at high temperatures and pressures without catalysts, the only processes of commercial importance involve low-temperature alkylation conducted in the presence of either sulfuric or hydrofluoric acid. The reactions occurring in both processes are complex and the product has a rather wide boiling range. By proper choice of operating conditions, most of the product can be made to fall within the gasoline boiling range with motor octane numbers ranging from 88 to 94 and research octane numbers ranging from 94 to 99 [7].

1.1 Trends in Alkylation

Trends in alkylation process selection, design, and use accentuate product quality improvement, lower operating costs, and better environmental compatibility. Alkylate, octane, and yield are improved through better reactor performance. Better utilization of energy is effected by more efficient fractionation and heat integration, and waste effluents are minimized through improved handling [8].

Another significant trend is in the choice of process type. Since 1975, H_2SO_4 alkylation capacity has declined relative to HF such that it is now less than half the total capacity. Reasons for the greater use of HF processing include the following:

Significantly lower acid consumption

Overall lower operating costs

Less expensive regeneration plant cost and operating expenses

Demand for high octane alkylate is increasing with the shift to low-lead or no-lead gasoline and greater emphasis on motor octane. With high utility costs, the trend is to improve the reactor system to achieve higher octane at equivalent or lower isobutane-to-olefin ratios, contrary to former use of higher isobutane-to-olefin ratios for better quality product. Nevertheless, the yield, volatility, and octane number of the product are regulated by adjusting the temperature, acid/hydrocarbon ratio, and isoparaffin/olefin ratio.

1.2 Alkylation Variables

At the same operating conditions, the products from the hydrofluoric and sulfuric acid alkylation process are quite similar [6,9]. In practice, however, the plants are operated at different conditions and the products are different.

The more important variables for both processes are the following:

Reaction temperature

Acid strength

Isobutane concentration

Olefin space velocity

The **reaction temperature** has a greater effect in H_2SO_4 processes than in HF processes. Low temperatures mean higher quality. For sulfuric acid reactors, the normal temperature is from 40 to 50 degrees F. For hydrofluoric acid alkylation, temperature is less significant, and reactor temperatures are in the range of 70 to 100 degrees F.

Acid strength has varying effects on alkylate quality. In hydrofluoric acid alkylation, the highest octane number alkylate is attained in the 86% to 90% by weight acidity range. Commercial operations usually have acid concentrations between 83% to 92% HF. If the concentration of the acid becomes less than 88%, some of the acid must be removed and replaced with stronger acid. In HF units, the acid removed is redistilled and the polymerization products removed as a thick dark oil. The concentrated HF is recycled in the unit and the net consumption is about 0.3 lb per barrel of alkylate produced, which compares unfavorably with the sulfuric acid alkylation where the acid consumption ranges from 18 lb to 30 lb per barrel of alkylate produced.

Isobutane concentration is generally expressed in terms of isobutane/olefin ratio. High isobutane/olefin ratios increase octane number and yield and reduce side reactions and acid consumption. Commercially, the isobutane/olefin ratio on reactor charge varies from 5:1 to 15:1.

Olefin space velocity is defined as the volume of olefin charged per hour, divided by the volume of acid in the reactor. It represents one way of expressing reaction time. The model developed in this study, which represents a simplified way to approach the process, does not define this variable.

1.3 Description of an HF Alkylation Unit

A typical HF alkylation unit for butylene charge stocks (Figure 1) feeds the reactor a treated, dried olefinic stream mixed with recycled isobutane along with a dispersed acid catalyst. Heat of reaction is removed by cooling water. Acid/hydrocarbon emulsion exits the reactor and passes to a settler where emulsion separates into an HF phase, which is recirculated to the reactor, and a hydrocarbon phase, which is taken to the isostripper. Reactor effluent is separated in the isostripper into four different fractions: alkylate, normal butane, isobutane recycle, and a overhead stream. Heat required for this separation is the major utility cost of this process; therefore, fractionation conditions are selected to maximize use of low-level heat sources and to integrated heat supplies.

Overhead from the isostripper containing isobutane, propane, and HF is charged to the HF stripper. The HF stripper bottoms are treated and recovered, usually in an existing external depropanizer. An internal depropanizer is required in a unit processing C_3-C_4 olefin feed or if a

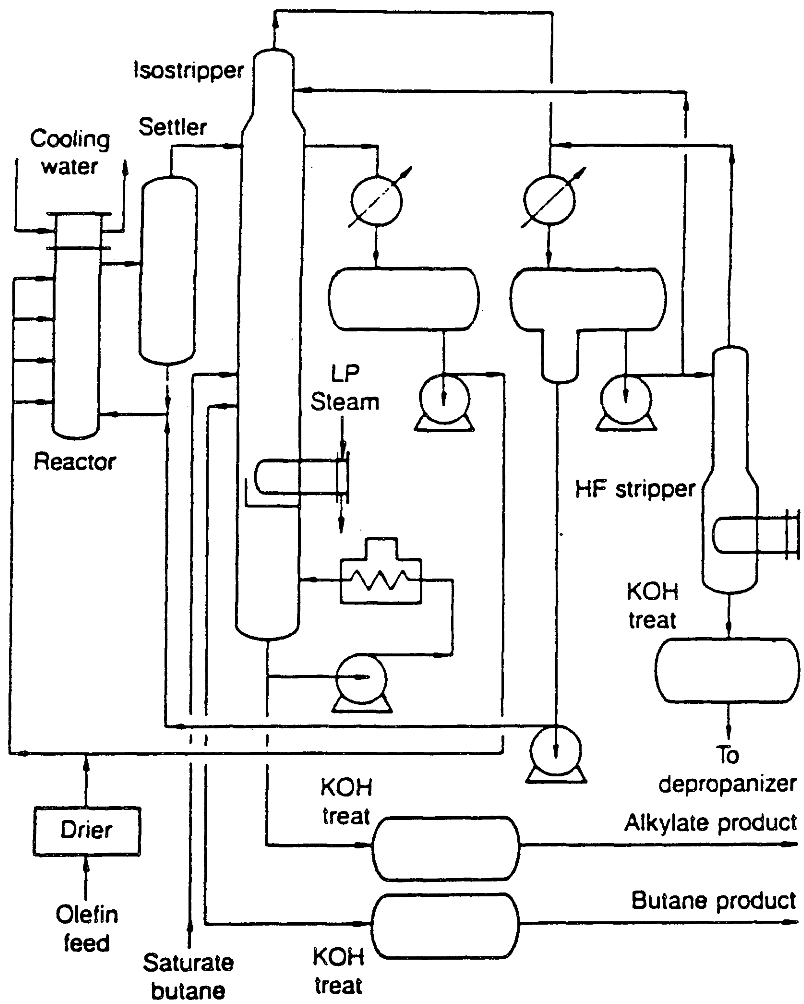

Figure 1: HF Alkylation Process

significant amount of propane enters the unit in the butylene feed.

All product streams are treated with KOH to guard against any acid traces leaving the unit because of upset conditions. Where propane or normal butane is used as LPG, defluorination facilities are provided to remove all traces of organic fluorides.

An acid regeneration column is provided in units for startup or in the event of feed contamination. During normal operations, acid purity is maintained by integral regeneration using the fractionation equipment in Figure 1.

Alkylate combines both high Research and Motor octane ratings. The high Motor octane rating is increasingly important since it contributes to premium gasoline performance in unleaded or low-lead gasolines. Additionally, alkylates have the advantage of being essentially 100% branched-chain paraffins, which is especially important where constraints limit the olefin, aromatic, or oxygen content of gasoline.

Chapter 2

PROBLEM DESCRIPTION

Different approaches have been used to design optimization under uncertainty. Process engineers normally handle uncertainties by adopting a conservative approach to design, selecting suitable safety factors based upon intuition and experience. If the design is to be optimized, the safety factors are merely incorporated into a deterministic model. With this approach, an experienced engineer can usually avoid bottlenecks, but sometimes at the expense of excessive overdesign.

Process design requires the selection and sizing of process equipment and the specification of normal operating conditions; a good design will achieve the desired performance in the most efficient and profitable way possible. The predicted plant performance and economics depend on both technological correlations and marketing and economic forecasts. Since these functions are subjected to uncertainties, the chosen design may differ significantly from the desired optimal design. Fortunately, once the process plant is built, the operating conditions actually used can normally be adjusted to counteract some of the undesirable effects of the uncertainty. Thus, the goal of the design engineer is to produce a design with enough flexibility to allow adjustment for most of the important uncertainties, yet avoid specifying excess capabilities which may prove to be unnecessary, once the operating conditions are adjusted to fit the actual plant performance and the observed market demands and prices.

Sauer, et al., [10] present the advantages of using digital computers in the field of process economic optimization. The paper outlines the necessary steps to construct a mathematical process model from ordinary operation correlations for an alkylation process.

The same correlations were used later by Malik and Hughes [5] who presented a procedure to optimize the alkylation optimization problem by direct analysis of the stochastic multistage decision problem.

Careful analysis of this model shows that the optimum profit determined by Sauer, et al., [10] was in error. This error was also present in a later paper on the same economic model by Malik and Hughes [5].

The alkylation model formulated by Sauer, et al., [10] represents the problem examined in this paper (see Table 1).

The purpose of this thesis is to define a search algorithm for a solution of this problem, then follow this by reformulating the original problem as a geometric programming type of problem showing that the sensitivity of the solution is facilitated greatly over the differential approach used by Malik and Hughes [5].

Table 1: Alkylation Process Model (Sauer, et al.)

Variables and Bounds: (10)	Minimum	Maximum
X_1 = olefin feed (bbls/d)	0.01	2,000
X_2 = isobutane recycle (bbls/d)	0.01	16,000
X_3 = acid addition rate (M lbs/d)	0.01	120
X_4 = alkylate yield (bbls/d)	0.01	5,000
X_5 = isobutane makeup (bbls/d)	0.01	2,000
X_6 = acid strength (w%)	85	93
X_7 = motor octane number	90	95
X_8 = ext. isobutane/olefin ratio	3	12
X_9 = acid dilution factor	1.2	4
X_{10} = F-4 performance number	145	162

Objective:

Maximize operating profit:

$$PHI = 0.063X_4*X_7 - 5.04*X_1 - 0.035*X_2 - 10*X_3 - 3.86*X_5$$

Subject to 7 equalities:

(1) $X_4 = X_1*(1.12 + 0.13167*X_8 - 0.006667*X_8^2)$

(2) $X_5 = 1.22*X_4 - X_1$

(3) $X_2 = X_1*X_8 - X_5$

(4) $X_6 = 89 + \{X_7 - (86.35 + 1.098*X_8 - 0.038*X_8^2)\}/0.325$

(5) $X_{10} = - 133 + 3*X_7$

(6) $X_9 = 35.82 - 0.222*X_{10}$

(7) $X_3 = 0.001*X_4*X_6*X_9/(98 - X_6)$

Chapter 3

COMPUTER MODEL

3.1 Definition of the Search Algorithm

The main reason for writing a search algorithm is to generate a reliable set of data which allows one to compare to the results attained with the geometric programming solution.

Of critical importance to this study is specifying the parts of the physical plant to be studied and optimized with the algorithm. A simplified process flow diagram of an alkylation process was presented in Figure 1. The model equations [10] are a means for representing the data and process relationships which have been acquired, but the similarity to alkylation is not complete because several simplifying assumptions were made in describing the process and in using the correlations. These assumptions, which were made basically to keep the model simple for practical reasons--easily accessible and reliable--are the following:

The olefin feed is assumed to be 100% butylene

Isobutane recycle and isobutane make-up are both assumed to be 100% isobutane

Fresh acid strength is assumed to be 93% by weight

Looking at the process flow diagram (Figure 1), there is a reactor into which olefin feed and isobutane make-up are introduced. Fresh acid is added to catalyze the reaction and spent acid is withdrawn. The hydrocarbon product from the reactor is fed to a fractionator, and isobutane is taken from the top and recycled back to the reactor. Alkylate product is withdrawn from the bottom of the fractionator.

3.2 The Independent Variables

These variables include those that can be referred to as the controllable variables. They can be controlled by the operator by changing a set point on an automatic controller. These are X_1 (olefin feed in bbls/d), X_7 (motor octane number), and X_8 (external isobutane/olefin ratio). The other independent variables over which there is no control include the relative humidity of the outside air, ambient temperature, and temperature of cooling water to the process.

3.3 Variables Determination for Alkylation Process

The first step in building the search algorithm is to define starting values for the independent variables. These values correspond to the following:

1. The upper bound for variable X_1 (olefin feed in bbls/d), which can be controlled easily since it can be seen as a valve that regulates the feed stream.
2. The upper bound for the motor octane number (X_7) which makes sense, since the higher the octane number and yield of the final product, the higher the profits derived from sales.

3. The value for X_8 (external isobutane/olefin ratio) is not easily defined "a priori," but according to industrial practice, the alkylation unit has to be protected against dangerously low isobutane/olefin ratios [11]. This suggests that a feasible region for X_8 could be in its upper range (between 9 and 12).

Once the values for the independent variables are defined, the next step is to write an algorithm which calculates the values for the dependent variables according to the limitations imposed by the feasible region (see constraints in Table 1). The search algorithm is written in BASIC (see Appendix A). Figure 2 represents a flow diagram of the different calculations performed by the search program.

3.4 Results of the Search Algorithm

In order to have an idea of the possible range of values for the independent variables which satisfy all the constraints (Table 1), a simple algorithm was written and the results presented in Appendix B. These results reduce the starting values for the bounds corresponding to the variable X_8 from 3 to 12 to 9 to 12 . This new range includes all the possible combinations which satisfy the constraints and simultaneously gives a positive value for the profit function (objective function).

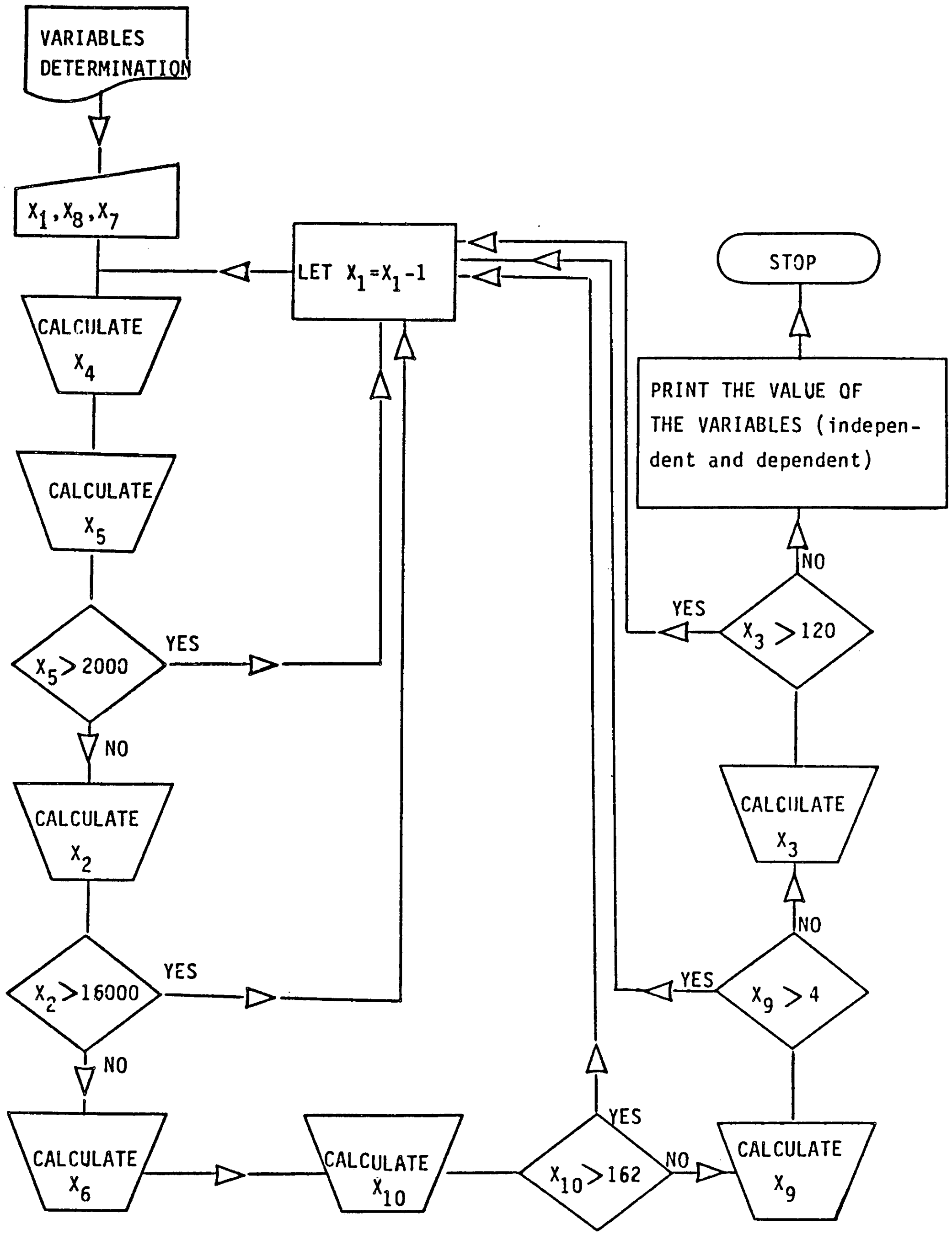

Figure 2: Flow Diagram for the Search Algorithm

Chapter 4

FORMULATION AS A GEOMETRIC PROGRAMMING PROBLEM

The objective function represents the operating profit for an alkylation process which is expressed by the equation

$$P= 0.063*X_4*X_7 - 5.04*X_1 - 0.035*X_2 - 10*X_3 - 3.86*X_5 \qquad (4.1)$$

subject to 7 equalities (see Table 1)

In order to simplify the problem, each one of the seven equalities was substituted in the objective function. The process is presented in detail as follows:

First, we define a new variable, P(4), as

$$P(4) = 1.12 + 0.13167*X_8 - 0.006667*X_8^2 \qquad (4.2)$$

$$X_4 = X_1*P(4) \qquad (4.3)$$

Substituting in eq. (4.1),

$$P = .063*X_1*P(4)*X_7 - 5.04*X_1 - .035*X_2 - 10*X_3 - 3.86*X_5 \qquad (4.4)$$

By letting $X_2 = X_1*X_8-X_5$ and substituting in eq. (4.4),

$$P = .063*X_1*P(4)*X_7 - 5.04*X_1 - .035*(X_1*X_8-X_5)$$

$$- 10*X_3 - 3.86*X_5 \tag{4.5}$$

Substituting,

$$X_5 = 1.22*X_4 - X_1 \tag{4.6}$$

In eq. (4.5),

$$P = .063*X_1*P(4)*X_7 - 5.04*X_1 - .035*(X_1*X_8 - 1.22*X_4 + X_1)$$
$$- 10*X_3 - 3.86*(1.22*X_4 - X_1) \tag{4.7}$$

Substituting the equation for X_3 in eq. (4.7),

$$X_3 = .001*X_4*X_6*X_9/(98 - X_6) \tag{4.8}$$

$$P = .063*X_1*P(4)*X_7 - 5.04*X_1 - .035*(X_1*X_8-1.22*X_4 + X_1)$$
$$- .01*(X_1*P(4)*X_6*X_9)/(98 - X_6)$$
$$- 3.86*(1.22*X_1*P(4) - X_1) \tag{4.9}$$

Factorizing X_1 out of eq. (4.9),

$$P = X_1*\{.063*P(4)*X_7 - 5.04 - .035*[X_8 - 1.22*P(4) + 1]$$
$$- .01*[P(4)*X_6*X_9/(98 - X_6)]$$
$$- 3.86*[1.22*P(4) - 1]\} \tag{4.10}$$

Rearranging terms in eq. (4.10),

$$P = X_1*[- 1.215 - 4.6665*P(4) + .063*P(4)*X_7 - .035*X_8 - .01*P(4)*X_6*X_9/(98 - X_6)] \quad (4.11)$$

Substituting (4.2) in eq. (4.11),

$$P = X_1*[- 1.215 - 4.6665*(1.12 + .13167*X_8 - .006667*X_8^2) + .063*(1.12 + .13167*X_8 - .006667*X_8^2)*X_7 - .035*X_8 - .01*(1.12 + .13167*X_8 - .006667*X_8^2)*X_6*X_9/(98 - X_6)] \quad (4.12)$$

Expanding eq. (4.12),

$$P = X_1*[- 1.215 - 4.6665*(1.12) - .13167*X_8 + 4.6667*X_8^2*(.006667) + .063*(1.12)*X_7 + .13167*(.063)*X_8*X_7 - .063*(.006667)*X_8^2*X_7 - .035*X_8 - .01*(1.12)*X_6*X_9/(98 - X_6) - .01*(.13167)*X_8*X_6*X_9/(98 - X_6) + .01*(.006667)*X_8^2*X_6*X_9*(98 - X_6)] \quad (4.13)$$

Since

$$X_9 = 35.82 - .222*(- 133 + 3*X_7) \quad (4.14)$$

Substituting eq.(4.14) in (4.13),

$$P = X_1*\{- 1.215 - 4.6665*(1.12) - 4.6665*(.13167)*X_8$$
$$+ 4.6665*(.006667)*X_8{}^2 + .063*(1.12)*X_7$$
$$+ .13167*(.063)*X_8*X_7 - .063*(.006667)*X_8{}^2*X_7$$
$$- .035*X_8$$
$$- .01*1.12*X_6*[35.82 + .222*133 - .222*3*X_7]/(98 - X_6)$$
$$- .01*.13167*X_8*X_6*[35.82 + .222*(133)$$
$$- .222*(3)*X_7]/(98 - X_6)$$
$$+ .01*.006667*X_8{}^2*X_6*[35.82 + .222*133$$
$$- .222*3*X_7]/(98 - X_6)\} \qquad (4.15)$$

Multiplying terms in eq. (4.15),

$$P = X_1*\{- 6.44148 - .649438*X_8 + .031112*X_8{}^2$$
$$+ .07056*X_7 + .008295*X_8*X_7 - .00042*X_7*X_8{}^2$$
$$- .01*1.12*X_6*[35.82 + .222*133 - .222*3*X_7]/(98 - X_6)$$
$$- .01*.13167*X_8*X_6*[35.82 + .222*133$$
$$- .222*3*X_7]/(98 - X_6)$$
$$+ .01*.006667*X_8{}^2*X_6*[35.82 + .222*133$$
$$- .222*3*X_7]/(98 - X_6)\} \qquad (4.16)$$

Letting

$$P(6) = 98 - X_6 \tag{4.17}$$

$$X_6 = 98 - P(6) \tag{4.18}$$

and substituting in eq.(4.16),

$$\begin{aligned} P = \; & X_1*\{- 6.44148 - .649438*X_8 + .031112*X_8^2 \\ & + .07056*X_7 + .008295*X_8*X_7 - .00042*X_7*X_8^2 \\ & + [- .01*(1.12)*35.82*98 - .01*(1.12)*.222*133*98 \\ & + .01*(1.12)*.222*98*3*X_7]/P(6) + .01*(1.12)*35.82 \\ & + .01*(1.12)*(.222)*133 - .01*(1.12)*(.222)*3*X_7 \\ & + [-.01*.13167*X_8*98*35.82 \\ & - .01*.13167*X_8*98*.222*133 \\ & + .01*(.13167)*X_8*98*(.222)*3*X_7]/P(6) \\ & + .01*(.13167)*X_8*35.82 + .01*(.13167)*X_8*.222*133 \\ & - .01*(.13167)*X_8*(.222)*3*X_7 \\ & + [.01*.006667*X_8^2*98*35.82 \\ & + .01*.006667*X_8^2*98*.222*133 \\ & - .01*.006667*X_8^2*98*.222*3*X_7]/P(6) \\ & - .01*.006667*X_8^2*35.82 - .01*.006667*X_8^2*.222*133 \\ & + .01*(.006667)*X_8^2*(.222)*3*X_7\} \end{aligned} \tag{4.19}$$

Multiplying terms in eq. (4.19),

$$P = X_1*\{(-\ 39.316032 - 32.407738 + .731002*X_7)/P(6)$$
$$+ .401184 + .330691 - .007459*X_7$$
$$+ (-\ 4.622091*X_8 - 3.809935*X_8 + .085938*X_7*X_8)/P(6)$$
$$+ .047164*X_8 + .038877*X_8 - .000877*X_7*X_8$$
$$+ (.234036*X_8^2 + .192913*X_8^2 - .004351*X_7*X_8^2)/P(6)$$
$$- .002388*X_8^2 - .001968*X_8^2 + .000044*X_7*X_8^2$$
$$- 6.44148 - .649438*X_8 + .031112*X_8^2 + .07056*X_7$$
$$+ .008295*X_8*X_7 - .00042*X_7*X_8^2\} \quad (4.20)$$

Simplifying eq. (4.20),

$$P = X_1*\{(-\ 71.723770 + .731002*X_7)/P(6)$$
$$+ (-\ 8.432066*X_8 + .085938*X_7*X_8)/P(6)$$
$$+ (.426949*X_8^2 - .004351*X_7*X_8^2)/P(6)$$
$$+ .731875 - .007459*X_7 + .086041*X_8 - .000877*X_7*X_8$$
$$- .004356*X_8^2 + .000044*X_8^2*X_7 - 6.44148$$
$$- .649438*X_8 + .031112*X_8^2 + .07056*X_7$$
$$+ .008295*X_8*X_7 - .00042*X_7*X_8^2\} \quad (4.21)$$

Rearranging eq.(4.21),

$$P = X_1*\{-\ 71.723770/P(6) + .731002*X_7/P(6)$$

$$- 8.432066*X_8/P(6) + .085938*X_8*X_7/P(6)$$
$$+ .426949*X_8^2/P(6) - .004351*X_7*X_8^2/P(6)$$
$$- 5.709605 + .063101*X_7 - .563397*X_8 + .007418*X_7*X_8$$
$$+ .026756*X_8^2 - .000376*X_7*X_8^2\} \quad (4.22)$$

Rearranging eq. (4.22),

$$P = X_1/P(6)*\{- 71.723770 + .731002*X_7 - 8.432066*X_8$$
$$+ .085938*X_7*X_8 + .426949*X_8^2 - .004351*X_7*X_8^2\}$$
$$+ X_1*\{- 5.709605 + .063101*X_7 - .563397*X_8$$
$$+ .007418*X_7*X_8 + .026756*X_8^2$$
$$- .000376*X_7*X_8^2\} \quad (4.23)$$

Equation (4.23) represents the new form of the objective function which has 12 terms and 4 variables (X_1, X_7, X_8, and P(6)), where X_1, X_7, and X_8 are independent variables.

Paying special attention to the first six terms in eq. (4.23), it can be seen that these are proportional to each other on the following form:

$$- 71.723770/.731002 = - 98.117064 = - 98.12$$
$$- 8.432066/.085938 = - 98.118015 = - 98.12$$
$$.426949/- .004351 = - 98.126638 = - 98.12$$

The reason for this fixed ratio has to do with the chemical reaction ocurring in alkylation, where the molar relation between the reactants is a constant. In order to keep the reaction forward, and avoid undesired subproducts, this relation is fixed. This implies that the first 6 terms of eq. (4.23) can be expressed as

$$P = X_1/P(6)*\{(\underbrace{-\ 71.723770 - 8.432066*X_8 + .426949*X_8^2}_{\text{always negative}})$$

$$\underbrace{*[1 - (1/98.12)*X_7]\}}_{\text{always positive}} \qquad (4.24)$$

In order to maximize profits (P), since the variable X_1 is always positive, the variable X_7 has to be fixed at its upper bound (X_7 = 95) in order to make this term as small as possible. Since P(6) = 98 - X_6, it implies that the variable X_6 has to be fixed at its lower bound (X_6 = 85). Then, the value for the variable P(6), after X_6 has been fixed, is P(6) = 13 .

Looking at the second 6 terms of eq. (4.23), it can be seen that

$$\underbrace{-\ 5.709605 - .563397*X_8 + .026756*X_8^2}_{\text{always negative}}$$

$$\underbrace{+\ .063101*X_7 + .007418*X_7*X_8 - .000376*X_7*X_8^2}_{\text{always positive}}$$

Because the goal is to maximize profits (P), it is necessary to make the positive terms as big as possible. In order to accomplish that, the variable X_7 has to be fixed at its upper bound ($X_7 = 95$), which is in agreement with the analysis from the first six terms. At this point, nothing conclusive can be said about the variable X_8.

Once X_6 has been fixed to its lower bound ($X_6 = 85$), the variable X_7 can be expressed as a function of X_8 (See Table 1) as following:

$$X_6 = 89 + [X_7 - (86.35 + 1.098*X_8 - .038*X_8^2)]/.325 \qquad (4.25)$$

By substituting $X_6 = 85$ in eq. (4.25) and solving for X_7,

$$X_7 = 85.05 + 1.098*X_8 - .038*X_8^2 \qquad (4.26)$$

By substituting P(6) = 13 and eq. (4.26) in eq. (4.23),

$$P = X_1/13*\{-\ 71.723770 - .731002*(85.05 + 1.098*X_8 - .038*X_8{}^2)$$
$$- 8.432066*X_8 + .085938*X_8*(85.05 + 1.098*X_8 - .038*X_8{}^2)$$
$$+ .426949*X_8{}^2$$
$$- .004351*X_8{}^2*(85.05 + 1.098*X_8 - .038*X_8{}^2)\}$$
$$+ X_1*\{-\ 5.709605 + .063101*(85.05 + 1.098*X_8 - .038*X_8{}^2)$$
$$- .563397*X_8 + .007418*X_8*(85.05 + 1.098*X_8 - .038*X_8{}^2)$$
$$+ .026756*X_8{}^2$$
$$- .000376*X_8{}^2*(85.05 + 1.098*X_8 - .038*X_8{}^2)\} \qquad (4.27)$$

Rearranging terms in eq. (4.27),

$$P = X_1*\{-5.517213 - 4.782440 - .061742*X_8 + .002137*X_8{}^2$$
$$- .648620*X_8 + .562233*X_8 + .007258*X_8{}^2 - .000251*X_8{}^3$$
$$+ .032842*X_8{}^2 - .028466*X_8{}^2 - .000367*X_8{}^3 + .000013*X_8{}^4$$
$$- 5.709605 + 5.366740 + .069285*X_8 - .002398*X_8{}^2$$
$$- .563397*X_8 + .630901*X_8 + .008145*X_8{}^2 - .000282*X_8{}^3$$
$$+ .026756*X_8{}^2 - .031979*X_8{}^2 - .000413*X_8{}^3 + .000014*X_8{}^4\} \qquad (4.28)$$

Simplifying eq. (4.28),

$$P = X_1*\{ - 10.642518 - .011340*X_8 + .014295*X_8{}^2$$
$$- .001313*X_8{}^3 + .000027*X_8{}^4 \} \qquad (4.29)$$

The substitution of the new value for the variable P(6) and the expression for X_7 (eq. 4.26) in eq. (4.23) reduces the complexity of the original problem from 12 terms and 4 variables to 5 terms and only one variable (X_8). This new simplified form of the objective function (P) can be solved by geometric programming (GP). Since GP as a mathematical tool can be used to solve minimization problems, eq. (4.29) can be expressed as

$$MAX\ P = MIN\ (-P)$$

$$MIN\ (-P) = X_1*\{\ 10.642518 + .011340*X_8 - .014295*X_8^2 + .001313*X_8^3 - .000027*X_8^4\ \} \quad (4.30)$$

Since X_1 is always positive, and it is a factor multiplying the whole expression, it can be left out of the equation for solving purposes. It is important to enhance the fact that the goal at this stage of the problem is to determine the value for the variable X_8 which satisfies the initial goal--maximize profits--.The new form of the objective function is expressed as

$$MIN\ P' = .011340*X_8 - .014295*X_8^2 + .001313*X_8^3 - .000027*X_8^4 \quad (4.31)$$

Following the rules for geometric programming resolution, degrees of difficulty (DD) are

DD = # of terms - # of variables - 1

= 4 - 1 - 1

= 2

which implies the solution is not optimal.

In order to get the value for the variable X_8, four subproblems from eq. (4.31) with zero degree of difficulty are solved

$$P'_1 = .011340{*}X_8 - .014295{*}X_8^2 \quad (4.32)$$

$$P'_2 = .011340{*}X_8 - .000027{*}X_8^4 \quad (4.33)$$

$$P'_3 = .001313{*}X_8^3 - .014295{*}X_8^2 \quad (4.34)$$

$$P'_4 = .001313{*}X_8^3 - .000027{*}X_8^4 \quad (4.35)$$

Solving eq. (4.32),

$$\text{MIN } P'_1 = .011340{*}X_8 - .014295{*}X_8^2$$

<u>RULE 2:</u>

$$d_1 - d_2 = \text{sigma } (\pm) \quad (4.36)$$

$$d_1 - 2d_2 = 0 \quad (4.37)$$

From eq. (4.36) and (4.37),

sigma = +1 , $d_1 = 2$, $d_2 = 1$

RULE 1:

$$P'_1{}^* = sigma*[(.011340/d_1)^{d1}*(.014295/d_2)^{d2}]^{sigma} \quad (4.38)$$

Making the proper substitutions,

$$P'_1{}^* = (.011340/2)^2*(.014295/1)^1 \quad (4.39)$$

$$P'_1{}^* = .002249$$

RULE 3:

$$P'_1{}^* = .011340*X_8/2 = .014295*X_8{}^2/1 = .002249 \quad (4.40)$$

where

$$X_8 = .396642$$

Repeating the same general procedure, eq. (4.33), (4.34), and (4.35) are solved, obtaining the following values for the variable X_8

$X_8 = 4.717694$

$X_8 = 7.258043$

$X_8 = 36.472091$

The values for the variable X_8 are substituted in eq. (4.29) and the results are

<u>Variable X_8</u>	<u>$P*X_1$ Values (eq. 4.29)</u>
.396642	- 10.644848
4.717694	- 10.502348
7.258043	- 10.398870
36.472091	- 7.966150

Since profits (P) have to be maximized, according to the trend in values of the variable X_8 and its influence on eq. (4.29), it is clear that X_8 has to be fixed to its upper bound in order to maximize P (higher values of X_8 imply more positive values for P). Further analysis of eq. (4.29) and its change in value with respect to X_8 indicates that the higher value for P in eq. (4.29) is obtained when $X_8 = 10.54$.

A different approach is presented, where the basic difference is the substitution of P(6) = 13 in eq. (4.23), without substituting X_7 for eq. (4.26). This substitution reduces the complexity of the original problem from 12 terms and 4 variables to 6 terms and 3 variables. Eq. (4.23) can be rewritten as

$$P = X_1*(- 11.226818 + .119332*X_7 - 1.212017*X_8 + .014029*X_7*X_8 - .000711*X_7*X_8^2 + .059598*X_8^2) \quad (4.41)$$

Rearranging eq. (4.41),

$$P = X_1*[(- 11.226818 + .119332*X_7) + (- 1.212017 + .014029*X_7)*X_8 + (.059598 - .000711*X_7)*X_8^2] \quad (4.42)$$

The solution for eq. (4.42) is accomplished by using the information from eq. (4.24) (X_7 = 95). The new expression for the objective function ignoring X_1 is

$$P = .109722 + .1207379*X_8 - 7.946998*(10^{-3})*X_8^2 \quad (4.43)$$

Equation (4.43) can be solved by geometric programming as a maximization problem,

$$\text{MAX } P = .1207379*X_8 - 7.946998*(10^{-3})*X_8^2 \quad (4.44)$$

Following the rules for geometric programming resolution, degrees of difficulty (DD) is

$$DD = \# \text{ of terms} - \# \text{ of variables} - 1$$
$$= 2 - 1 - 1$$
$$= 0$$

which implies the solution is optimal.

RULE 2:

$$d_1 - d_2 = \text{sigma} (\pm 1) \quad (4.36)$$
$$d_1 - 2d_2 = 0 \quad (4.37)$$

From eq. (4.37),

$$d_1 = 2d_2$$

Substituting in eq.(4.36),

$$2d_2 - d_2 = \text{sigma} , \text{ which implies sigma} = 1$$

Then

$$d_1 = 2, \quad d_2 = 1$$

RULE 1:

$$P^* = sigma*[(.1207379/d_1)^{d1} * (.007946/d_2)^{-d2}]^{sigma} \quad (4.45)$$

Making the proper substitutions,

$$P^* = (.1207379/2)^2*(.007946)^{-1} \quad (4.46)$$

$$= .4585895$$

RULE 3:

$$P^* = .1207379*X_8/2 = .007946*X_8^2 = .4585895 \quad (4.47)$$

where

$$X_8 = 7.5964471$$

By substituting $X_8 = 7.6$ in the equation for X_6 (see Table 1),

$$X_6 = 89+[X_7 - (86.35 + 1.098*X_8 - .038*X_8^2)]/.325 \quad (4.25)$$

$$X_6 = 96.69$$

Since the upper bound for X_6 is 93 ($85 < X_6 < 93$), the value for X_6 is set to its upper bound ($X_6 = 93$). Then, the value for the variable X_8 is recalculated by trial and error in equation (4.25):

$$93 = 89 + [95 - (86.35 + 1.098*X_8 - .038*X_8^2)]/.325 \qquad (4.48)$$

where $X_8 = 10.56$

The variable X_8 represents the external isobutane/olefin ratio, which in industrial practice is expressed as an integer number (from 3:1 to 12:1).

The agreement between the two approaches taken verifies the validity of the solution for X_8 ($X_8 = 11$).

Solution

From what has gone before we now assert that $X_7 = 95$ (its upper bound) by the examination of the entire 12 terms of eq. (4.23) discussed before. From our two different approaches using geometric programming we assert that $X_8 = 11$. This is done as customary industrial practice requires an integer isobutane/olefin ratio. We now recall that there is an equality in the original model relating X_6, X_7, and X_8 (equation 4 in Table 1) restated here as

$$X_6 = 89 + [X_7 -(86.35 + 1.098*X_8 - .038*X_8^2)]/.325 \qquad (4.49)$$

Substituting $X_7 = 95$ and $X_8 = 11$ from above we find that from eq. (4.49) that X_6 = 92.59999

If we now substitute the above values of X_6, X_7, X_8 into eq. (4.23) (the original model restated as a function of X_1, X_7, X_8, and P(6)), we get from eq. (4.23)

$$\text{Profit} = X_1*(\ .0956096059) \tag{4.50}$$

Remembering that X_1 is upper bounded by 2000 bbls/day, it is tempting to simply assert, using eq. (4.50), that maximum Profit is $191.22.

Before doing this, however, one last bit of analysis is required. We recall, from Table 1, that the bounds on X_1, X_4, X_5, and X_2 are respectively

$$.01 \leq X_1 \leq 2{,}000\ , \tag{4.51}$$

$$.01 \leq X_4 \leq 5{,}000\ , \tag{4.52}$$

$$.01 \leq X_5 \leq 2{,}000\ ,\ \text{and} \tag{4.53}$$

$$.01 \leq X_2 \leq 16{,}000 \tag{4.54}$$

We further recall that these variables are related by the equalities from Table 1

$$X_4 = X_1*(\ 1.12 + .13167*X_8 - .006667*X_8^2\ ) \tag{4.55}$$

$$X_5 = 1.22*X_4 - X_1 \tag{4.56}$$

$$X_2 = X_1*X_8 - X_5 \tag{4.57}$$

If we substitute $X_8 = 11$ in the above equalities we have

$$X_4 = 1.761663*X_1 \tag{4.58}$$

$$X_5 = 2.149228*X_1 \tag{4.59}$$

$$X_2 = 9.850771*X_1 \tag{4.60}$$

Now, if $X_4 \leq 5000$, eq. (4.58) implies that $X_1 \leq 2838.227$, which is within the upper bound of $X_1 = 2000$. We then look at eq. (4.59), which implies that $X_1 = 1740.297$. Finally we examine $X_2 \leq 16{,}000$ and eq. (4.60) which shows that to satisfy the bounds on X_2, $X_1 \leq 1624.238$. If we now have the largest allowed value of $X_1 = 1624.238$, we may assert that our analysis would result in a maximum profit, from eq. (4.50), of

$$P = (1624.238)*(.0956096059) = \$155.27 \tag{4.61}$$

Our profit calculation (objective function eq. 4.1) is checked by our computer algorithm of Chapter 3. By setting $X_8 = 11$, $X_7 = 95$, and a starting value for $X_1 = 2000$, the computer algorithm defined in Chapter 3 determines as an optimal value of the objective function P=155.27, with a redefined value for $X_1 = 1624$ bbls/d. This solution satisfies all the equality constraints (presented in Table 1). Table 2 presents the results obtained from the search algorithm and the analysis with GP solution. Table 3 presents the results for the profit calculation for both methods. Figure 3 is the graphical solution for the optimum profit determination from the search algorithm. In this graph, X_1 = 1624 and X_7 is plotted against profit for values of X_8 = 9, 10, 11, and 12.

Table 2: Independent Variable Values for GP and Search Algorithm Methods

Independent Variables	GP Solution	Search Algorithm
X_1 (bbls/d)	1624.238	1624
X_7 (motor octane #)	95	94.5
X_8 (ext iC4/olefin)	11	11

Table 3: Profit Calculation, Comparison between GP and Search Algorithm Solutions

	Profit ($)	% Difference
GP	155.27	
SEARCH ALGORITHM	179.11*	
		15.35%

* This difference is caused by the derived value of $X_7 = 95$ using GP, and the Search Algorithm using a value of $X_7 = 94.5$.

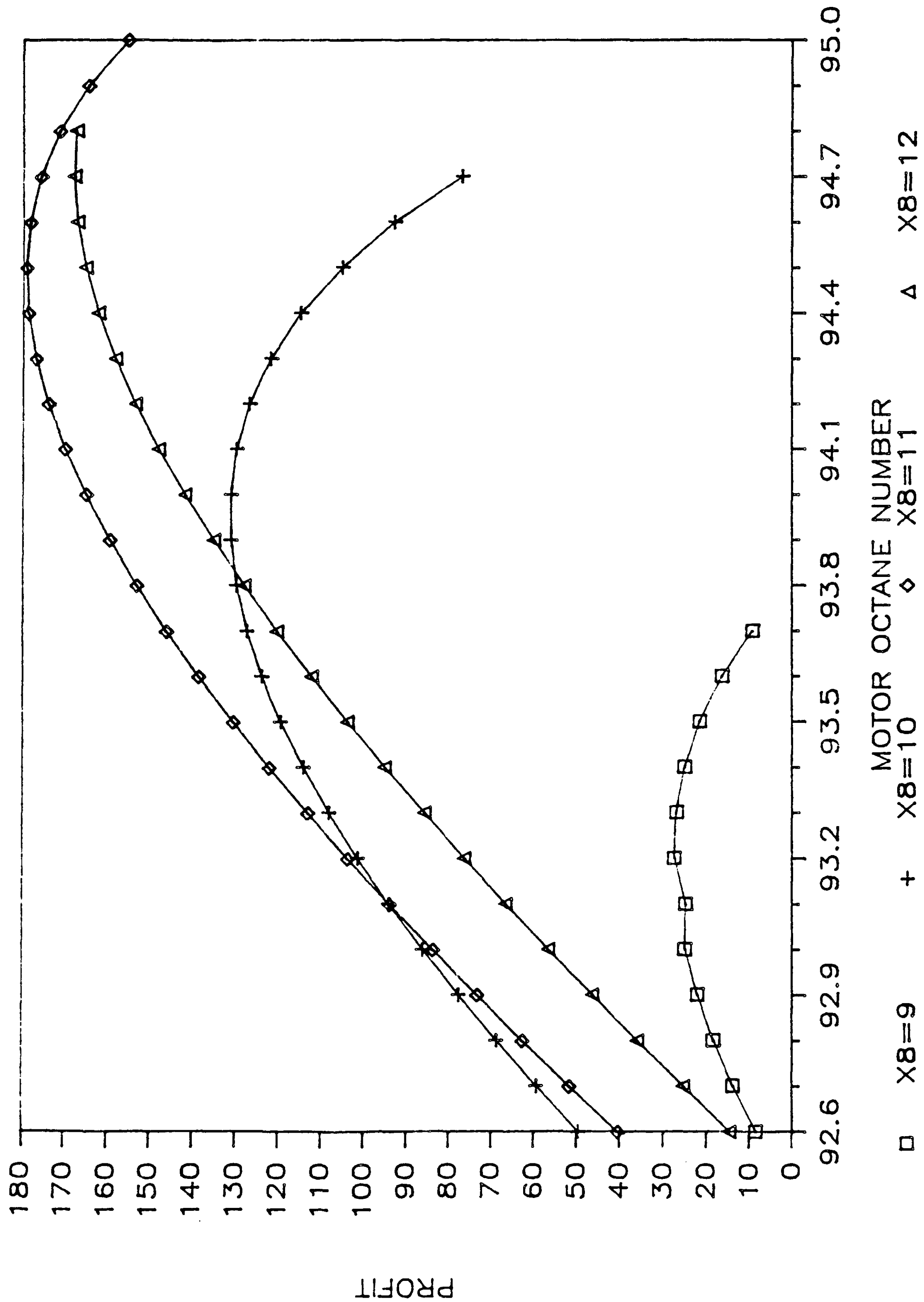

Figure 3: Optimum Profit Determination

Chapter 5

CONCLUSIONS

The use of Geometric Programming (GP) as an optimization technique for this specific process (alkylation) has been demonstrated to reduce the complexity of the initial expression for the profit function. The initial problem contained 42 terms and 10 variables, giving 31 degrees of difficulty (DD) including upper and lower bounds. The problem was reduced to 6 terms and 4 variables with only 1 DD. Furthermore, GP provided an idea of which ones were the crucial variables to be considered for the design process. An obvious suggestion for further study is the derivation of the unit process GP deltas (% contributions to cost) for this model.

The original problem in ten variables was reduced to a problem in X_1, X_7, X_8, and X_6. Using GP, bounds were established on X_7, X_6, and X_8. Final analysis showed an appropiate upper bound on X_1.

The optimum value for the profit function determined by analysis and GP differs from the maximum value attainable calculated by the search algorithm in 15% (See Table 3).

The primary contribution of this thesis is the demonstration that GP and solid analysis, without the use of computers, can result in (a) considerable insight into operating practice of a complex process such as alkylation and (b) final operating parameters and profits well within accepted industrial practice for the industry. This is an indication for greater potential application of GP to design optimization of chemical processes in the oil industry.

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APPENDIXES

A. SEARCH ALGORITHM

```
10     '---------------------------------------------------'
20     'VARIABLES DETERMINATION FOR ALKYLATION PROCESS'
30     '---------------------------------------------------'
40     '
41     '
42     'INDEPENDENT VARIABLES'
43     '*********** *********'
44     '
50     'X(1) = OLEFIN FEED (bbls/day)'
60     'X(8) = EXT. ISOBUTANE/OLEFIN RATIO'
61     'X(7) = MOTOR OCTANE NUMBER'
62     '
65     PRINT "X(1)=";
70     INPUT X(1)
75     PRINT "X(8)=";
80     INPUT X(8)
82     PRINT "X(7)=";
85     INPUT X(7)
90     '
100    'CALCULATE X(4) = ALKYLATE YIELD (bbls/day)
110    '----------------------------------------'
111    '
120    LET X(4) = X(1)*(1.12+.13167*X(8)-.006667*X(8)^2)
150    '
160    'CALCULATE X(5) = ISOBUTANE MAKEUP (bbls/day)'
170    '-----------------------------------------'
171    '
180    LET X(5)=1.22*X(4)-X(1)
190    IF X(5)>2000 THEN 210
203    GOTO 260
210    LET X(1)=X(1)-1
220    GOTO 120
230    '
240    'CALCULATE X(2) = ISOBUTANE RECYCLE (bbls/day)'
250    '------------------------------------------'
251    '
260    LET X(2)=X(1)*X(8)-X(5)
270    IF X(2)>16000 THEN 300
280    GOTO 350
300    LET X(1)=X(1)-1
310    GOTO 120
320    '
```

```
330     'CALCULATE X(6) = ACID STRENGTH (w%)'
340     '----------------------------------'
341     '
350     LET X(6)=89+(X(7)-(86.35+1.098*X(8)-.038*X(8)^2))/.325
370     '
380     'CALCULATE X(10) = F-4 PERFORMANCE NUMBER'
390     '----------------------------------------'
391     '
400     LET X(10)=-133+3*X(7)
410     IF X(10)>162 THEN 430
425     GOTO 480
430     LET X(1)=X(1)-1
440     GOTO 120
450     '
460     'CALCULATE X(9) =  ACID DILUTION FACTOR'
470     '--------------------------------------'
471     '
480     LET X(9)=35.82-.222*X(10)
490     IF X(9)>4 THEN 510
500     GOTO 560
510     LET X(1)=X(1)-1
520     GOTO 120
530     '
540     'CALCULATE X(3) = ACID ADDITION RATE (M lbs/day)'
550     '-----------------------------------------------'
551     '
560     LET X(3)=.001*X(4)*X(6)*X(9)/(98-X(6))
562     IF X(3)>120 THEN 650
566     '
567     'PROFIT DETERMINATION
568     '-------------------
569     '
571     LET P=.063*X(4)*X(7)-5.04*X(1)-.035*X(2)-10*X(3)-3.86*X(5)
572     '
575     PRINT
580     PRINT "VALUE FOR X(1)=";X(1)
585     PRINT "VALUE FOR X(2)=";X(2)
590     PRINT "VALUE FOR X(3)=";X(3)
595     PRINT "VALUE FOR X(4)=";X(4)
600     PRINT "VALUE FOR X(5)=";X(5)
605     PRINT "VALUE FOR X(6)=";X(6)
610     PRINT "VALUE FOR X(7)=";X(7)
620     PRINT "VALUE FOR X(8)=";X(8)
630     PRINT "VALUE FOR X(9)=";X(9)
640     PRINT "VALUE FOR X(10)=";X(10)
645     PRINT "VALUE FOR PROFIT P=";P
650     END
```

```
'COMPUTER RUN USING THE OPTIMAL VALUES AS AN EXAMPLE
_
_
_
RUN
X(1)=? 2000
X(8)=? 11
X(7)=? 94.5

VALUE FOR X(1)= 1624
VALUE FOR X(2)= 15997.65
VALUE FOR X(3)= 90.45176
VALUE FOR X(4)= 2860.941
VALUE FOR X(5)= 1866.348
VALUE FOR X(6)= 91.06153
VALUE FOR X(7)= 94.5
VALUE FOR X(8)= 11
VALUE FOR X(9)= 2.409001
VALUE FOR X(10)= 150.5
VALUE FOR PROFIT P= 179.1123
Ok_
```

B. VARIABLES VALUE FOR OPTIMUM PROFIT

```
5    OPEN "B:THES.DAT" FOR OUTPUT AS #2
10  '==================================================================
20  'ALKYLATION PROCESS:POSSIBLE COMBINATIONS FOR VARIABLES X(7) & X(8)
30  '==================================================================
35  LPRINT "            X(7)            X(8)            PROFIT   "
37  LET K=K+1
40     '
50     '-----------------------------------
60     'DEFINE RANGE FOR X(7)
70     '-----------------------------------
80     '
90     FOR X7=92.6 TO 95 STEP .1
100            '
110            '-----------------------------------
120            'DEFINE RANGE FOR X(8)
130            '-----------------------------------
140            '
150            FOR X8=3 TO 12
160            '
165            '-----------------------------------------------------
170            'CALCULATE X(6) FOR STARTING VALUES OF X(7) & X(8)
180            '-----------------------------------------------------
190            '
200            LET X6=89+(X7-(86.35+1.098*X8-.038*X8^2))/.325
210            LET P6=98-X6
220            '
230            '-------------------------------------------------------
240            'DEFINE PROFIT FUNCTION "P" FROM THREE SUBSTITUTIONS
250            '-------------------------------------------------------
260            '
270            LET R1=-71.72377#/P6+.731002*X7/P6-5.709605+.063101*X7
280            LET R2=-8.432066/P6+.085938*X7/P6-.563397+.007418*X7
290            LET R3=.426949/P6-.004351*X7/P6+.026756-.000376*X7
300            LET P=R1+R2*X8+R3*X8^2
310            '
```

```
320              '---------------------------------------------------
330              'PRINT ONLY POSITIVE VALUES FOR PROFIT FUNCTION "P"
340              '---------------------------------------------------
350              '
360              IF P>0 THEN GOTO 390
370              GOTO 450
380              END IF
382              LPRINT "#";K;":    ";
390              LPRINT "          ";X7;"            ";X8;"             ";P
395              LET K=K+1
400              '
410              '-----------------------------------------------
420              'NEXT VALUE FOR X(8) AND X(7)
430              '-----------------------------------------------
440              '
450              NEXT X8
460      NEXT X7
470  END
```

X(7)	X(8)	PROFIT
92.6	3	4.99645
92.6	10	2.542019E-02
92.6	11	.0208205
92.7	3	3.974327
92.7	9	2.110183E-03
92.7	10	3.108484E-02
92.7	11	.0277282
92.79999	3	3.311813
92.79999	9	5.171716E-03
92.79999	10	3.651333E-02
92.79999	11	3.448278E-02
92.79999	12	5.153299E-03
92.89999	3	2.848605
92.89999	9	7.800102E-03
92.89999	10	4.168683E-02
92.89999	11	4.107255E-02
92.89999	12	1.249534E-02

92.99999	3	2.507374
92.99999	9	9.953827E-03
92.99999	10	4.658318E-02
92.99999	11	4.748601E-02
92.99999	12	1.971453E-02
93.09999	3	2.246195
93.09999	4	40.51615
93.09999	9	1.158434E-02
93.09999	10	5.117673E-02
93.09999	11	5.370653E-02
93.09999	12	2.680105E-02
93.19999	3	2.040378
93.19999	4	11.94221
93.19999	9	1.263836E-02
93.19999	10	5.544067E-02
93.19999	11	5.972165E-02
93.19999	12	3.374422E-02
93.29999	3	1.874457
93.29999	4	7.088507
93.29999	9	1.305237E-02
93.29999	10	5.934215E-02
93.29999	11	6.550753E-02
93.29999	12	.0405311
93.39999	3	1.738225
93.39999	4	5.086656
93.39999	9	1.275468E-02
93.39999	10	6.284625E-02
93.39999	11	.0710485
93.39999	12	.0471499
93.49999	3	1.624681
93.49999	4	3.996616
93.49999	9	1.166478E-02
93.49999	10	6.591487E-02
93.49999	11	7.631934E-02
93.49999	12	5.358666E-02
93.59998	3	1.528873
93.59998	4	3.312742
93.59998	9	9.683013E-03
93.59998	10	6.849903E-02
93.59998	11	8.129716E-02

93.59998	12	5.982459E-02
93.69998	3	1.447181
93.69998	4	2.844963
93.69998	9	6.699473E-03
93.69998	10	7.054651E-02
93.69998	11	8.595079E-02
93.69998	12	6.584573E-02
93.79998	3	1.376924
93.79998	4	2.505786
93.79998	9	2.583474E-03
93.79998	10	7.199866E-02
93.79998	11	9.024769E-02
93.79998	12	7.162946E-02
93.89998	3	1.316042
93.89998	4	2.249327
93.89998	5	17.63058
93.89998	10	7.278395E-02
93.89998	11	9.415012E-02
93.89998	12	7.715082E-02
93.99998	3	1.262953
93.99998	4	2.049222
93.99998	5	8.284714
93.99998	10	7.282007E-02
93.99998	11	.0976159
93.99998	12	.0823862
94.09998	3	1.21641
94.09998	4	1.889231
94.09998	5	5.504165
94.09998	10	7.201273E-02
94.09998	11	.1005965
94.09998	12	8.730411E-02
94.19998	3	1.175415
94.19998	4	1.758804
94.19998	5	4.172816
94.19998	10	7.024926E-02
94.19998	11	.103033
94.19998	12	9.187114E-02
94.29998	3	1.139165
94.29998	4	1.650795
94.29998	5	3.394266
94.29998	10	6.739849E-02
94.29998	11	.1048597
94.29998	12	9.604728E-02

94.39997	3	1.107006
94.39997	4	1.560187
94.39997	5	2.884998
94.39997	10	6.330013E-02
94.39997	11	.1060008
94.39997	12	9.979069E-02
94.49997	3	1.078398
94.49997	4	1.483357
94.49997	5	2.527068
94.49997	6	258.1792
94.49997	10	5.776459E-02
94.49997	11	.1063627
94.49997	12	.1030442
94.59997	3	1.052892
94.59997	4	1.417629
94.59997	5	2.262653
94.59997	6	12.63799
94.59997	10	5.055505E-02
94.59997	11	.1058353
94.59997	12	.105746
94.69997	3	1.030113
94.69997	4	1.360967
94.69997	5	2.060049
94.69997	6	6.685954
94.69997	10	.0413872
94.69997	11	.1042923
94.69997	12	.1078228
94.79996	3	1.009741
94.79996	4	1.311812
94.79996	5	1.900423
94.79996	6	4.643329
94.79996	10	2.990878E-02
94.79996	11	.1015757
94.79996	12	.1091951
94.89996	3	.9915049
94.89996	4	1.268936
94.89996	5	1.771895
94.89996	6	3.614105
94.89996	10	1.567108E-02
94.89996	11	9.749866E-02
94.89996	12	.1097583
94.99996	3	.9751766
94.99996	4	1.231374
94.99996	5	1.666591
94.99996	6	2.996226
94.99996	11	9.182638E-02
94.99996	12	.1093843