4

ALKYLATION PROCESS

OPTIMIZATION

In this chapter we describe a model for optimization of the operation of a chemical process common in the petroleum industry. The model seeks to determine the optimum set of operating conditions for the process, based on a mathematical model of the process, a profit function to be maximized, and a set of starting conditions. Most chemical processes can be represented by nonlinear relationships without discontinuities, and they are usually constrained by numerous restrictions on the operating ranges of the variables. The interrelationships among the variables are sufficiently complicated so that changing one variable usually results in changes in a number of the other variables.

The model was described by Sauer, Colville, and Burwick [3], and the process relationships used in the model are based on those given by Payne [2]. The solution procedure used by Sauer, Colville, and Burwick for optimizing the model is a reduction of the nonlinear problem to a series of linear programming problems, which is described by Colville [1]. We have formulated the model as a direct nonlinear programming model with mixed nonlinear inequality and equality constraints and a nonlinear criterion function. The formulation is described in this chapter.

4.1 DESCRIPTION OF ALKYLATION PROCESS MODEL

Description of the Process and Variables

A simplified process flow diagram of an alkylation process is given in Figure 4.1. There is a reactor in which olefin feed and isobutane makeup are introduced. Fresh acid is added to catalyze the reaction, and spent acid is withdrawn. The hydrocarbon product from the reactor is fed into a
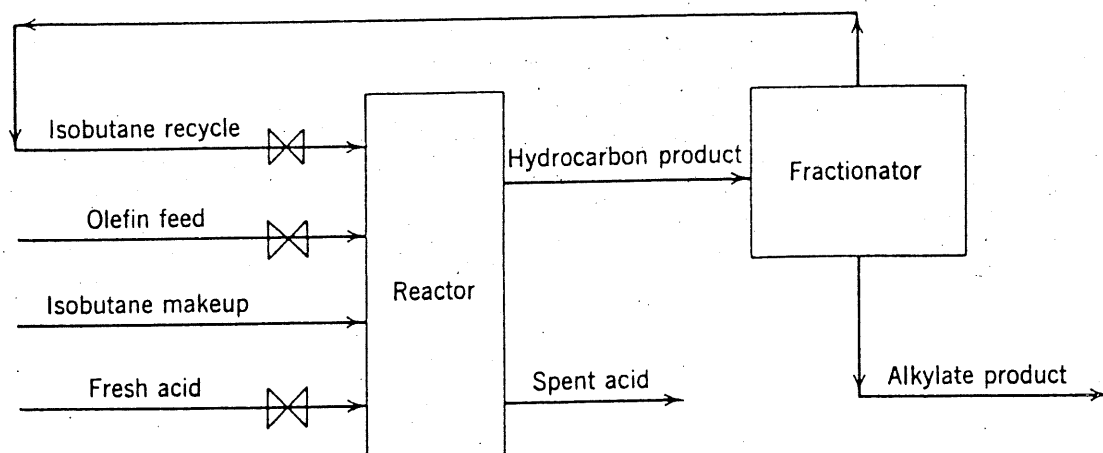
Figure 4.1 Simplified Alkylation Process Flow Diagram

fractionator, and isobutane is taken from the top of the fractionator and recycled back into the reactor. Alkylate product is withdrawn from the bottom of the fractionator. Several of the simplifying assumptions are that the olefin feed is 100 per cent butylene, isobutane makeup and isobutane recycle are 100 per cent isobutane, and fresh acid strength is 98 per cent by weight.

Payne [2] discusses the process variables and their relationships with each other. Some of the relationships involve material balances, while some are correlations between variables within certain ranges, described by linear or nonlinear regressions. We shall develop equality constraints for material balances, and inequality constraints for regression relationships.

It is convenient to define independent and dependent variables in formulating the model, although mathematically the nonlinear programming problem treats the variables alike. The independent variables are the controllable or "knob" variables, the values of which are determined by the operator by changing set points on automatic control instruments. On the process flow diagram these variables are indicated by butterfly valves (-▷◁-). Changes in the values of these independent variables induce changes throughout the process. The independent variables are the olefin feed rate in barrels per day, the isobutane recycle in barrels per day, and the fresh acid addition rate in thousands of pounds per day. There are other independent variables, not in the model, which we assume have been appropriately taken care of, such as relative humidity of outside air and temperature of cooling water in the process.

The dependent variables can be divided into three classes: (a) economically significant variables, (b) performance indices, and (c) supporting variables, defined and used when building the model. The economically significant dependent variables are alkylate yield in barrels per day and isobutane makeup in barrels per day. The other dependent variables are acid strength

by weight per cent, motor octane number (also economically significant), external isobutane-to-olefin ratio, acid dilution factor, and F-4 performance number.

Relationships Used in Determining Constraints

We start off by defining the 10 variables to be considered in the model, which have already been mentioned and are mathematically related in this section. We define

x_1 = olefin feed (barrels per day),
x_2 = isobutane recycle (barrels per day),
x_3 = acid addition rate (thousands of pounds per day),
x_4 = alkylate yield (barrels per day),
x_5 = isobutane makeup (barrels per day),
x_6 = acid strength (weight per cent),
x_7 = motor octane number,
x_8 = external isobutane-to-olefin ratio,
x_9 = acid dilution factor,
x_{10} = F-4 performance number.

Values to be taken on by the variables are all bounded from below and above. The independent variables x_1, x_2, and x_3 and the dependent variables x_4 and x_5 have limitations imposed by the economic situation under analysis. For example, only 2000 barrels per day of olefin feed, x_1, may be available for use in the process. These bounds will be included as constraints in the model. Similarly, the performance indices are required to lie within certain specified ranges because of the physical relationships of the process, and these bounds will be included as constraints.

We give the equations for the dependent variables as functions of independent variables and of other dependent variables. The alkylate yield, x_4, is a function of the olefin feed, x_1, and the external isobutane-to-olefin ratio, x_8. The relationship is determined by a nonlinear regression holding at reactor temperatures between 80 to 90°F and reactor acid strength by weight per cent of 85 to 93. The regression equation is

$$x_4 = x_1(1.12 + .13167x_8 - .00667x_8{}^2).$$

The isobutane makeup, x_5, can be determined by a volumetric reactor balance. The alkylate yield, x_4, equals the olefin feed, x_1, plus the isobutane makeup, x_5, less shrinkage. The volumetric shrinkage can be expressed as .22 volume per volume of alkylate yield. The balance is then

$$x_4 = x_1 + x_5 - .22x_4,$$

or

$$x_5 = 1.22x_4 - x_1.$$

The acid strength by weight per cent, x_6, can be derived from an equation that expresses acid addition rate, x_3, as a function of alkylate yield, x_4, acid dilution factor, x_9, and acid strength by weight per cent, x_6. The addition acid is assumed to have acid strength of 98. The equation is

$$1000x_3 = \frac{(x_4)(x_9)(x_6)}{(98 - x_6)}.$$

Rearranging, we obtain acid strength as a function of acid addition rate, alkylate yield, and acid dilution factor:

$$x_6 = \frac{98,000x_3}{x_4 x_9 + 1000x_3}.$$

The motor octane number, x_7, is a function of the external isobutane-to-olefin ratio, x_8, and the acid strength by weight per cent, x_6. The relationship holds for the same reactor temperatures and acid strengths as for alkylate yield, x_4. The equation determined by nonlinear regression is

$$x_7 = 86.35 + 1.098x_8 - .038x_8^2 + .325(x_6 - 89).$$

The external isobutane-to-olefin ratio, x_8, is equal to the sum of the isobutane recycle, x_2, and the isobutane makeup, x_5, divided by the olefin feed, x_1. The equation is

$$x_8 = \frac{x_2 + x_5}{x_1}.$$

The acid dilution factor, x_9, can be expressed as a linear function of the F-4 performance number, x_{10}. A curve is approximated by the linear regression equation

$$x_9 = 35.82 - .222x_{10}.$$

The last dependent variable is the F-4 performance number, x_{10}, which may be expressed as a linear function of the motor octane number, x_7. The linear regression equation is

$$x_{10} = -133 + x_7.$$

The above relationships give the dependent variables in terms of the independent variables and the other dependent variables. All of the relationships must hold for the process to be in balance. In addition to the above

Table 4.1 Lower and Upper Bounds on Selected Dependent Variables

Dependent Variable	Minimum Limit	Maximum Limit
x_6, acid strength (weight per cent)	85	93
x_7, motor octane number	90	95
x_8, external isobutane-to-olefin ratio	3	12
x_9, acid dilution factor	1.2	4
x_{10}, F-4 performance number	145	162

relationships, there are lower and upper bounds to be imposed on the variables. The independent variables have these bounds imposed by the capability of the physical plant and/or the economic situation being analyzed. These will be specified in the example. The dependent variables alkylate yield, x_4, and isobutane makeup, x_5, also are affected by the economic situation and other general conditions. But the dependent variables x_6, x_7, x_8, x_9, and x_{10} have bounds that are directly related to the physical process. Table 4.1 shows the minimum and maximum limits for these variables.

Profit Function

The profit function is defined in terms of alkylate product or output value minus feed and recycle costs. Operating costs not reflected in the function we assumed not to vary among possible process setups.

Define the value and cost parameters to be used in the profit function:

c_1 = alkylate product value (dollars per octane-barrel),

c_2 = olefin feed cost (dollars per barrel),

c_3 = isobutane recycle costs (dollars per barrel),

c_4 = acid addition cost (dollars per thousand pounds),

c_5 = isobutane makeup cost (dollars per barrel).

The total profit per day, to be maximized, is

$$\text{Profit} = c_1 x_4 x_7 - c_2 x_1 - c_3 x_2 - c_4 x_3 - c_5 x_5.$$

Specification of Model

Define lower and upper bounds on the variables

$x_j^{(l)}$ = lower bound on the jth variable,

$x_j^{(u)}$ = upper bound on the jth variable,

where $j = 1, \ldots, 10$.

Regression analysis was used to formulate the relationships for x_4, x_7, x_9, and x_{10} in terms of the other variables. Exact models were used for the relationships for x_5, x_6, and x_8. For the former variables we use two inequality constraints that specify a range within which the true value can be approximated by the estimated value. For the latter variables one equality constraint is used.

Thus for the relationship

$$x_4 = f(x_1, x_8)$$

we use

$$f(x_1, x_8) - d_{4_l} x_4 \geq 0,$$
$$-f(x_1, x_8) + d_{4_u} x_4 \geq 0,$$

where d_{4_l} and d_{4_u} are the lower and upper values establishing the percentage difference of the estimated from the true value. An example that illustrates

how these inequalities work may be seen by setting $d_{4_l} = \frac{9}{10}$ and $d_{4_u} = \frac{10}{9}$. The inequalities

$$\tfrac{9}{10}x_4 \leq f(x_1, x_8) \leq \tfrac{10}{9}x_4$$

reduce to

$$f(x_1, x_8) - \tfrac{9}{10}x_4 \geq 0,$$

$$-f(x_1, x_8) + \tfrac{10}{9}x_4 \geq 0.$$

With these preliminaries taken care of, we write the nonlinear programming model for maximizing profit per day of the alkylation process by setting the independent variables equal to the optimal values as follows. Choose x_j $(j = 1, \ldots, 10)$ to

$$\text{maximize } c_1 x_4 x_7 - c_2 x_1 - c_3 x_2 - c_4 x_3 - c_5 x_5$$

subject to the constraints

$$x_j^{(l)} \leq x_j \leq x_j^{(u)}, \qquad j = 1, \ldots, 10,$$

$$[x_1(1.12 + .13167x_8 - .00667x_8^2)] - d_{4_l}x_4 \geq 0,$$

$$-[x_1(1.12 + .13167x_8 - .00667x_8^2)] + d_{4_u}x_4 \geq 0,$$

$$[86.35 + 1.098x_8 - .038x_8^2 + .325(x_6 - 89)] - d_{7_l}x_7 \geq 0,$$

$$-[86.35 + 1.098x_8 - .038x_8^2 + .325(x_6 - 89)] + d_{7_u}x_7 \geq 0,$$

$$[35.82 - .222x_{10}] - d_{9_l}x_9 \geq 0,$$

$$-[35.82 - .222x_{10}] + d_{9_u}x_9 \geq 0,$$

$$[-133 + 3x_7] - d_{10_l}x_{10} \geq 0,$$

$$-[-133 + 3x_7] + d_{10_u}x_{10} \geq 0,$$

$$1.22x_4 - x_1 - x_5 = 0,$$

$$\frac{98,000x_3}{x_4 x_9 + 1,000x_3} - x_6 = 0,$$

$$\frac{x_2 + x_5}{x_1} - x_8 = 0.$$

The final element to be mentioned is the starting values that are input to the model. These represent a balanced or nearly balanced process that engineers have developed, which should be a feasible solution satisfying the constraints. It is not absolutely necessary, for some nonlinear programming procedures can determine their own feasible solutions, but good starting values can be very helpful in solving the nonlinear programming problem.

4.2 EXAMPLE OF ALKYLATION PROCESS MODEL APPLICATION

In this section we given the necessary data for an example of the model just described and discuss solution of the problem. The example is taken

Table 4.2 Lower and Upper Bounds on Variables, and Starting Values

Variable	Lower Bound	Upper Bound	Starting Value
x_1, olefin feed (barrels per day)	0	2,000	1,745
x_2, isobutane recycle (barrels per day)	0	16,000	12,000
x_3, acid addition rate (thousands of pounds per day)	0	120	110
x_4, alkylate yield (barrels per day)	0	5,000	3,048
x_5, isobutane makeup (barrels per day)	0	2,000	1,974
x_6, acid strength (weight per cent)	85	93	89.2
x_7, motor octane number	90	95	92.8
x_8, external isobutane-to-olefin ratio	3	12	8
x_9, acid dilution factor	1.2	4	3.6
x_{10}, F-4 performance number	145	162	145

from Sauer, Colville, and Burwick [3]. Lower and upper bounds on the variables are given in Table 4.2, which includes the bounds to be used in the particular situation being studied in addition to those previously specified for the physical process. Also given in Table 4.2 are starting values for the optimization procedure.

Parameters for profit from the sale of alkylate and costs of inputs required for production are given in Table 4.3. Using the starting values from Table 4.3,

$$\text{Profit} = (\$.063)(3,048)(92.8) - (\$5.04)(1,745) - (\$.035)(12,000)$$
$$- (\$10.00)(110) - (\$3.36)(1,974)$$
$$= \$872.$$

The final input parameters to be specified are the permissible error relationships for the inequality constraints on the regression relationships. Table 4.4 gives the lower and upper deviation parameters.

Table 4.3 Values of Profit and Cost Parameters

Profit and Cost Parameter	Value
c_1, alkylate product value	$.063 per octane-barrel
c_2, olefin feed cost	$5.04 per barrel
c_3, isobutane recycle cost	$.035 per barrel
c_4, acid addition cost	$10.00 per thousand pounds
c_5, isobutane makeup cost	$3.36 per barrel

Table 4.4 · Values of Deviation Parameters

Deviation Parameter	Value
d_{4_l}	99/100
d_{4_u}	100/99
d_{7_l}	99/100
d_{7_u}	100/99
d_{9_l}	9/10
d_{9_u}	10/9
d_{10_l}	99/100
d_{10_u}	100/99

The data in Tables 4.2, 4.3, and 4.4 are sufficient to allow application of the model described in the previous section. Values of the independent and dependent variables that maximize profit subject to the constraints are given in Table 4.5. Also listed are lower and upper bounds and starting values. The profit associated with the optimal solution is $1769 per day, an increase of $897 over that of the starting value.

Isobutane recycle, x_5, is at the upper limit in the optimal solution given above. To test the sensitivity of profits of the process to an increase in the availability of isobutane makeup, we increase the upper limit of x_5 by 10 per cent to 2200 barrels. We also arbitrarily increase the upper bound on fractionation capacity by 25 per cent to 20,000, to allow for more isobutane recycle if this will balance the process at a higher level of profit. The profit goes to $1946, an increase of $1074 over the starting value. Isobutane recycle x_5 is used at the limiting point of 2200 barrels, and isobutane recycle goes to 17,396 barrels, which shows the necessity for increasing the fractionation capacity to balance the increased isobutane makeup.

Table 4.5 · Optimal Solution of Example Problem

Variable	Lower Bound	Optimum Value	Upper Bound	Starting Value
x_1	0	1,698	2,000	1,745
x_1	0	15,818	16,000	12,000
x_3	0	54.1	120	110
x_4	0	3,031	5,000	3,048
x_5	0	2,000	2,000	1,974
x_6	85	90.1	93	89.2
x_7	90	95.0	95	92.8
x_8	3	10.5	12	8
x_9	1.2	1.6	4	3.6
x_{10}	145	154	162	145

References

[1] A. R. Colville, Jr., "Process Optimization Program for Non-linear Programming," unpublished paper, IBM Corporation, December 1964.

[2] R. E. Payne, "Alkylation—What You Should Know about This Process," *Petrol. Refiner*, **37**, 316–329 (1958).

[3] R. N. Sauer, A. R. Colville, Jr., and C. W. Burwick, "Computer Points the Way to More Profits," *Hydrocarbon Process. Petrol. Refiner*, **43**, 84–92 (1964).