A STUDY OF THE DEVELOPMENT OF A MEXICAN PETROCHEMICAL INDUSTRY USING MIXED-INTEGER PROGRAMMING

by

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ABSTRACT

A large interactive system such as the petrochemical industry requires a model that can account for the different interactions among units, providing at the same time a suitable mathematical representation of the variables of interest. In this work, a model for the development of a Mexican petrochemical industry is presented. The system is formulated as a Mixed-Integer Programming model, where installing a process is compared on an economic basis to importing its corresponding product. This formulation lets the model take economies-of-scale into account, which are shown to be a very decisive factor in the selection of chemical processes, since a simple linear model does not seem to provide an adequate tool for the planning and development of a Mexican petrochemical industry. A heuristic approach using multiple linear programs is also discussed.

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Introduction

The petrochemical industry can be viewed as a system that takes petroleum feedstocks, expands into a complex network of chemical processes, and finally converges in the manufacture of end-products such as rubbers, fibers, plastics and resins. These materials, in turn, serve specific uses in the economy, where they are consumed in the form of tires, toys, clothing, etc.

Data on different petrochemical processes are available (1), including mass balance coefficients, energy consumption and investment requirements. This information is based on commercial processes in current use in the U.S. A linear programming model for the development of the petrochemical industry has been formulated (2-4); the model is driven by exogenous demand for chemicals, coming out with an optimal structure of the industry, including:

a) the set of chemicals that should be produced, and

b) the technologies that should be used to manufacture those chemicals.

The assumptions of linearity are very nearly followed by mass balance and energy factors, but the investment term is highly nonlinear. To overcome this problem, an "optimal" plant size has been defined, formulating then a linear operating cost for such a plant. This seems to be good approximation for studies applied to the U.S. since these plants would be operating close enough to full capacity.

When planning the development of a Mexican petrochemical industry, however, interesting differences arise. First, this country has been continuously importing some of its petrochemicals, and secondly, the

levels of demand for chemicals are several orders of magnitude lower than those required in the U.S. This means that some of the optimal plants for the latter will not be the best choice for Mexico. Trevino and Rudd (5) considered some strategies for imports substitution, detecting the existence of a superior policy. The second factor described above, however, has not previously been taken into account.

In this paper, an approach for the development of a Mexican petrochemical industry using Mixed-Integer Programming (MIP) is described.

Formulation of the problem

Let N be the number of chemicals involved in the operation of M processes. In our Mexican model for the intermediate petrochemical industry $N = 131$ and $M = 182$. The problem from a Linear Programming (LP) viewpoint can be formulated by the following economic model:

$$\min_{F,X,I} \quad \sum_{i=1}^{N} F_i P_i + \sum_{j=1}^{M} C_j X_j + \sum_{i=1}^{N} I_i B_i$$

$$\text{s.t.} \quad F_i + \sum_{j=1}^{M} a_{ij} X_j + I_i \geq D_i \qquad (i=1,\ldots,N)$$

$$0 \leq F_i \leq S_i \qquad (i=1,\ldots,N)$$

$$X_j \geq 0 \qquad (j=1,\ldots,M)$$

$$I_i \geq 0 \qquad (i=1,\ldots,N)$$

where F_i is the exogenous feedstock i consumed at a local unit price P_i, and limited by supply availabilities S_i; C_j is the unit operating

cost of process j, and X_j is the level of operation of that process; I_i is the amount of imported material i at a unit cost B_i; D_i represents the exogenous demand for chemical i; and a_{ij} is an input-output coefficient that reflects the consumption/production of chemical i in process j.

This formulation implies that the operating cost of a plant has been taken as linear. Thus, C_j reflects a unit cost due to utilities and investment for each process j. The cost of raw materials is not included in C_j since it has been accounted for by the cost of upstream processes and exogenous materials. A more accurate model describes the operating cost by a fixed-charge function, such as that shown in Figure 1. This function represents the conditions that,

$$\text{Opn. cost} = 0 \quad \text{for} \quad X = 0, \quad \text{and}$$

$$\text{Opn. cost} = E^* + C^*X \quad \text{for} \quad X > 0$$

where E^* is a fixed investment, and C^* reflects the unit cost of energy consumed as utilities. It is well known that this function does not have a Linear Programming Minimization Model since it has a concave geometry (i.e. its epigraph is not convex) (6,7), but it can be represented by the following model:

$$\text{Opn. cost} = \min\ (E^*Y + C^*X)$$

$$\text{s.t.} \quad 0 \leq X \leq K \cdot Y$$

$$Y = 0 \text{ or } 1$$

where K is a valid upper bound (in this case, the capacity of a chemical process). The binary variable Y reflects the event of building

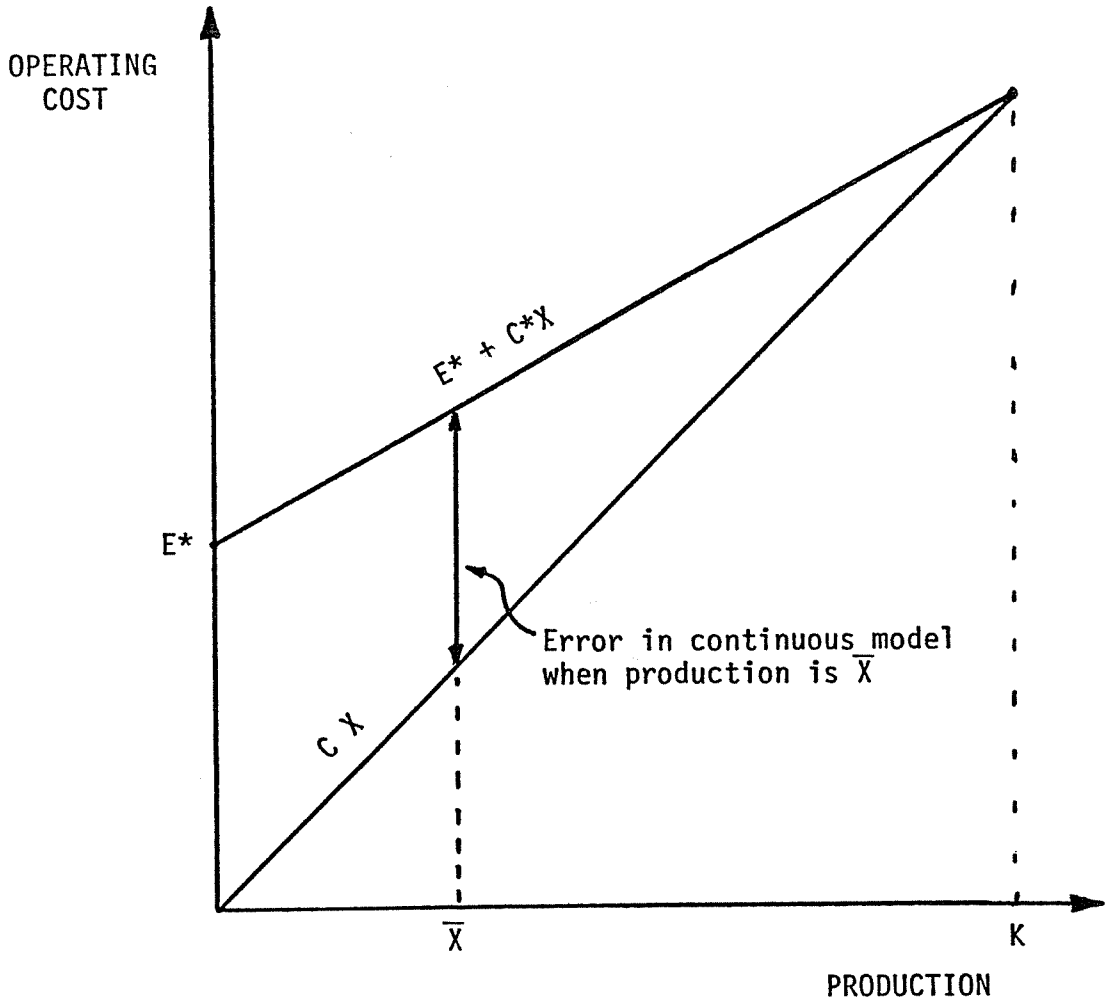


Figure 1. Modeling the operating cost via a fixed-charge function.

(Y=1) or not building (Y=0) a plant.

Under these circumstances, the problem can be reformulated via the following MIP:

$$\min_{F,X,I,Y} \quad \sum_{i=1}^{N} F_i P_i + \sum_{j=1}^{M} (E_j^* Y_j + C_j^* X_j) + \sum_{i=1}^{N} I_i B_i$$

$$\text{s.t.} \quad F_i + \sum_{j=1}^{M} a_{ij} X_j + I_i \geq D_i \qquad (i=1,\ldots,N)$$

$$0 \leq F_i \leq S_i \qquad (i=1,\ldots,N)$$

$$I_i \geq 0 \qquad (i=1,\ldots,N)$$

$$0 \leq X_j \leq K_j Y_j \qquad (j=1,\ldots,M)$$

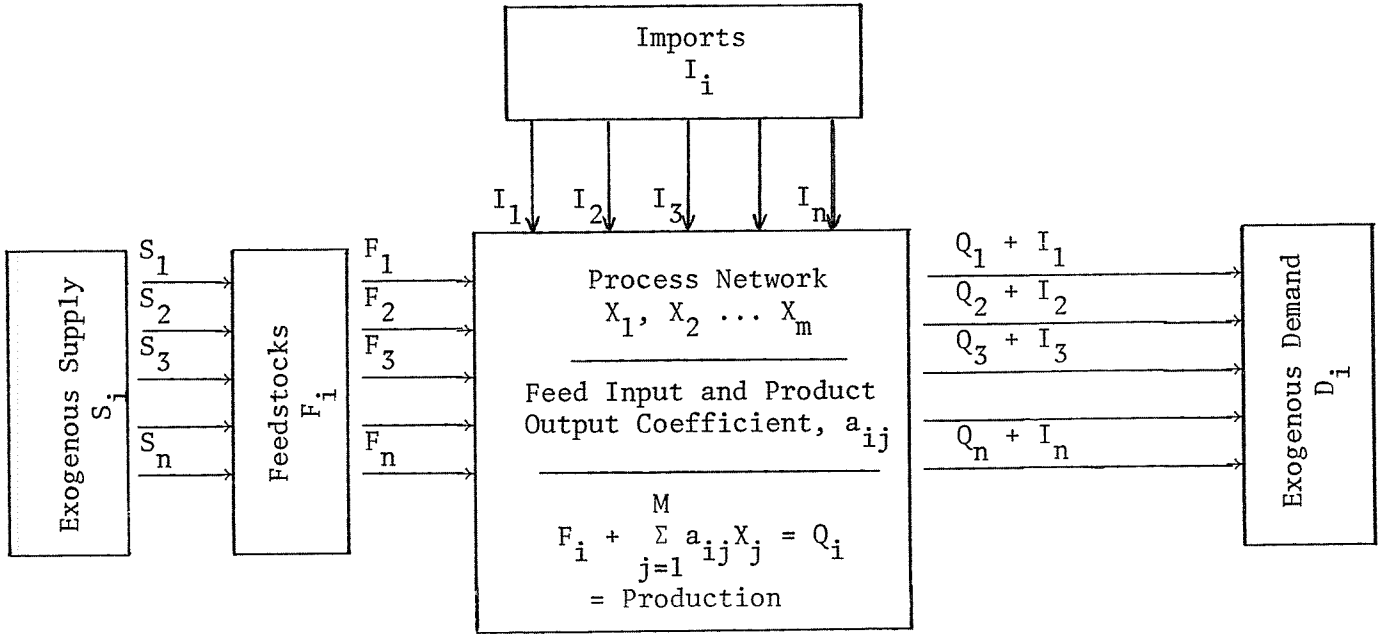
$$Y_j = 0 \text{ or } 1 \text{ for all } j.$$

The structure of this model is shown in Figure 2. The selection of importing a petrochemical or building a plant to produce it will strongly depend on the total demand for that product. With the present formulation, one can expect an economic break-even point where installing a chemical plant should be preferred to importing its corresponding product (see Figure 3). In other words, the plant should operate at adequate economies-of-scale to justify its investment. This effect cannot be detected if one uses LP.

Developing a Mexican petrochemical industry

The model formulated above was applied to get an ideal Mexican petrochemical industry for 1985. Demands for chemicals were obtained from reference (8). Chemical plant costs were projected using Plant Indexes reported by Chemical Engineering magazine (9). Projections of

Figure 2. Model Structure



MATERIAL BALANCE

BOUND CONSTRAINTS

Supply Limitations	Process Capacity Limitations	Demand Requirements
$F_i \leq S_i$	$X_j \leq K_j Y_j$	$D_i \leq Q_i + I_i$
	$Y_j = 0$ or 1	

OBJECTIVE FUNCTION

$$\text{Minimize Total Cost} = \min_{F,X,I,Y} \left[\sum_{i=1}^{N} P_i F_i + \sum_{j=1}^{M} (E_j^* Y_j + C_j^* X_j) + \sum_{i=1}^{N} I_i B_i \right]$$

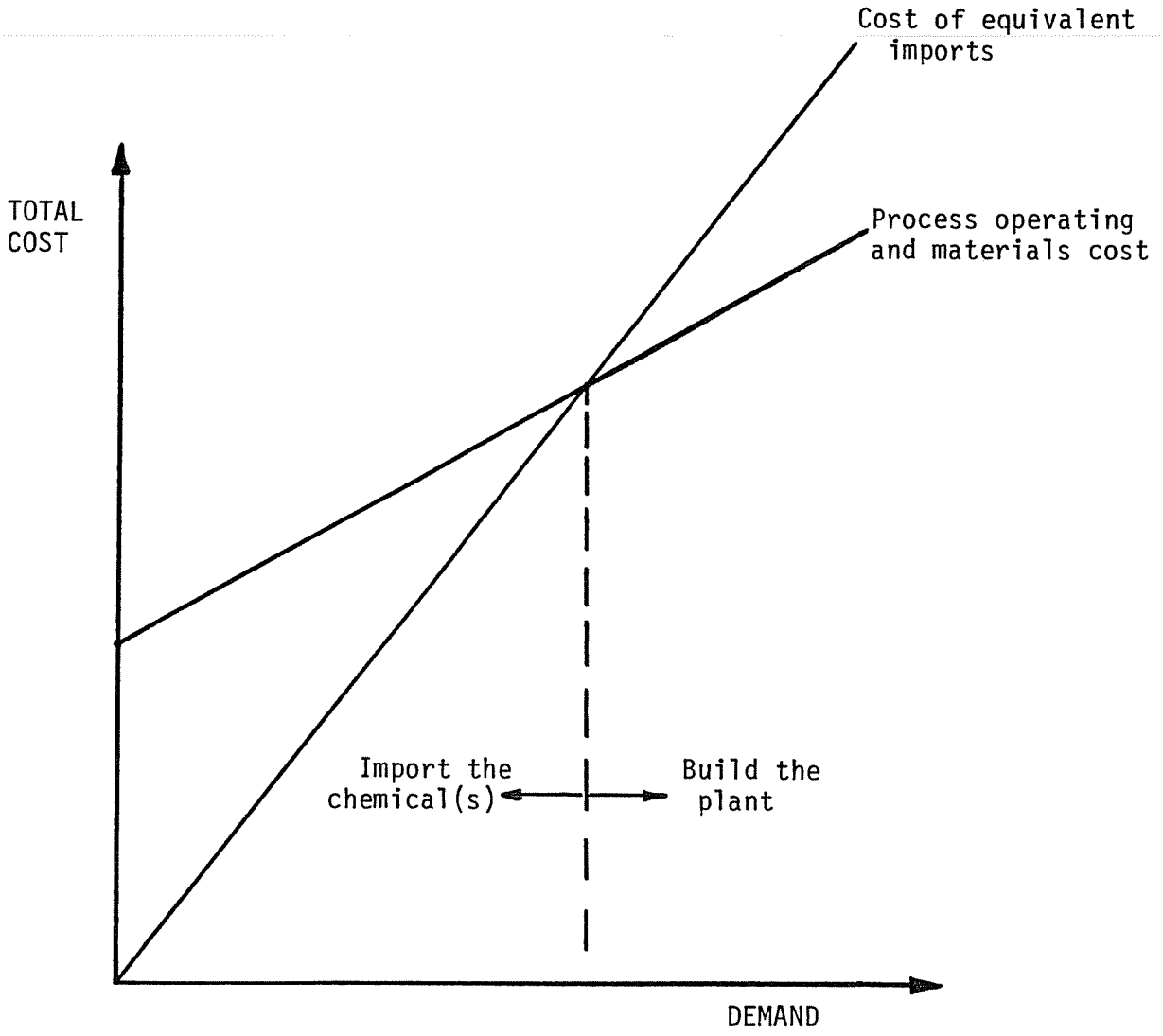


Figure 3. Economic comparison between building a chemical plant and importing its product.

international chemical prices given in Chemical Marketing Reporter (10) were used as import costs. The technologies included in the model are listed in Table 1. A depreciation factor of 10% and a return on investment of 25% were assumed; labor related costs were taken as 10% of the total investment.

Since applying MIP directly would require considerable computing time, an LP relaxation run was made first to get some basic information about the system, as well as to allow a comparison of the results of both techniques. The FMPS-LP routine (11) available on the Madison Academic Computing Center Univac 1110 was used for this purpose. The run took 8.42 seconds of CPU time, and the optimal value of the objective function was 4.126×10^9 \$/year. This yields a lower bound for the original problem. From the LP solution it is observed that 15 chemicals are to be imported, and 52 chemicals should be produced in the country; the list of these products and the technologies chosen to manufacture them is reported in Table 2. Imported materials include 96.3 KT of acetylene and 61.6 KT of terephtalic acid crude in addition to the amounts of these chemicals produced internally. Comparing the levels of production to the capacity of the selected processes, we notice the following:

a) 16 types of processes have a utilization factor of at least 80%; they seem likely to be installed, and we will consider them as continuous variables again in our MIP formulation,

b) 15 processes have a utilization factor lower than 20%; they seem impractical and their products should probably be imported. Therefore, these processes will not be included in our MIP formulation (i.e. $Y = 0$ for these processes), and

TABLE 1. CHEMICAL PROCESSES INCLUDED IN THE MODEL

NO.	PROCESS DESCRIPTION
1.	Acetaldehyde Via Ethylene (One-Step Oxidation)
2.	Acetaldehyde Via Ethylene (Two-Step Oxidation)
3.	Acetaldehyde Via Oxidation of Ethanol
4.	Acetic Acid Via Carbonylation of Methanol
5.	Acetic Acid Via Air Oxidation of Acetaldehyde
6.	Acetic Acid Via Oxidation of n-Butane
7.	Acetic Acid Via Oxidation of n-Butylenes
8.	Acetic Anhydride Via Oxidation of Acetaldehyde
9.	Acetic Anhydride Via Ketene and Acetic Acid
10.	Acetone Via V.P. Dehydrogenation of Isopropanol
11.	Acetone Via Oxidation of Propylene
12.	Acetylene From Residual Oil (Submerged Flame Process)
13.	Acetylene Via Hydration of Calcium Carbide
14.	Acetylene Via Pyrolysis of Methane
15.	Acetylene Via Pyrolysis of Naphtha
16.	Acetylene Via Pyrolysis of Ethane
17.	Acrolein Via Oxidation of Propylene
18.	Acrylamide Via Hydration of Acrylonitrile (Fixed Bed Catalyst)
19.	Acrylamide Via Hydration of Acrylonitrile (Suspended Catalyst)
20.	Acrylamide Via Sulfuric Acid Process
21.	Acrylic Acid Via Oxidation of Propylene
22.	Acrylic Acid Via Carbonylation of Acetylene
23.	Acrylonitrile Via Ammoxidation of Propylene
24.	Acrylonitrile Via Cyanation/Oxidation of Ethylene
25.	Adipic Acid from Cyclohexane
26.	Adipic Acid Via Cyclohexanol
27.	Adiponitrile Via Adipic Acid and Ammonia
28.	Adiponitrile Via Hydrodimerization of Acrylonitrile
29.	Allyl Alcohol Via Isomerization of Propylene Oxide
30.	Allyl Alcohol Via Acrolein and s-Butyl Alcohol
31.	Allyl Chloride Via Chlorination of Propylene

TABLE 1. (Cont'd)

NO.	PROCESS DESCRIPTION
32.	Ammonia from Natural Gas
33.	Ammonia from Naphtha
34.	Aniline Via Mononitrobenzene
35.	Aniline Via Ammonolysis of Cyclohexanol
36.	Aniline Via Phenol and Ammonia
37.	Benzene Via Hydrodealkylation of Toluene
38.	Benzene Via Disproportionation of Toluene
39.	Bisphenol-A Via Phenol and Acetone
40.	Butadiene Via Dehydrogenation of n-Butylenes
41.	Butadiene from n-Butylenes (Oxidative Dehydrogenation)
42.	Butadiene Via Dehydrogenation of n-Butane
43.	1,4-Butanediol Via Acetylene and Formaldehyde
44.	1,4-Butanediol from Butadiene
45.	1,4-Butanediol from Propylene, Chemical Grade
46.	1,4-Butanediol Via Propylene Oxide
47.	n-Butanol Via Propylene (Conventional Oxo)
48.	n-Butanol Via Propylene (Co-Phosphine Catalyst)
49.	n-Butanol Via Propylene (Rhodium Catalyst)
50.	s-Butanol Via Sulfonation of n-Butylenes
51.	Butyraldehyde Via Oxonation of Propylene
52.	Caprolactam Via Hexahydrobenzoic Acid
53.	Caprolactam Via Nitric Oxide Reduction Process
54.	Caprolactam Via Phenol Process
55.	Caprolactam from Cyclohexane
56.	Caprolactam Via Cyclohexanone and Hydroxylamine
57.	Carbon Monoxide from Natural Gas
58.	Carbon Monoxide from Naphtha
59.	Chlorine from Sodium Chloride (Electrolysis)
60.	Chlorobenzene Via Chlorination of Benzene
61.	Chlorobenzene Via Oxychlorination of Benzene
62.	Chloroprene Via Chlorination of Butadiene
63.	Chloroprene Via Dimerization of Acetylene

TABLE 1. (Cont'd)

NO.	PROCESS DESCRIPTION
64.	Cumene from Benzene and Propylene
65.	Cyclohexane Via Hydrogenation of Benzene
66.	Cyclohexanol Via Oxidation of Cyclohexane
67.	Cyclohexanol from Cyclohexane (Boric Acid Process)
68.	Cyclohexanol Via Oxidation of Cyclohexane
69.	Cyclohexanone Via Dehydrogenation of Cyclohexanol
70.	Cyclohexanone Via Cyclohexane
71.	Dimethyl Terephthalate from p-Xylene
72.	Dimethyl Terephthalate Via TPA
73.	Dinitrotoluene Via Nitration of Toluene
74.	Epichlorohydrin Via Allyl Chloride
75.	Ethanol Via Hydration of Ethylene
76.	Ethyl Acrylate Via Acrylic Acid
77.	Ethyl Acrylate Via Acrylonitrile
78.	Ethyl Acrylate Via Acetylene
79.	Ethylbenzene Via Benzene Alkylation
80.	Ethylene Via Ethane-Propane (50:50) Cracking
81.	Ethylene Via Gas Oil (High Severity) Cracking
82.	Ethylene Via Naphtha (High Severity) Cracking
83.	Ethylene Via Pyrolysis of Ethane
84.	Ethylene Via Pyrolysis of Propane
85.	Ethylene Via Naphtha (Low Severity) Cracking
86.	Ethylene Via Gas Oil (Low Severity) Cracking
87.	Ethylene Via Gas Oil (Medium Severity) Cracking
88.	Ethylene Via Hydrogenation of Acetylene
89.	Ethylene Via Dehydrogenation of Ethanol
90.	Ethylene Dichloride Via Chlorination of Ethylene
91.	Ethylene Dichloride Via Ethylene (Oxy-Chlorination)
92.	Ethylene Glycol Via Ethylene Oxide
93.	Ethylene Glycol Via Ethylene Oxidation

TABLE 1. (Cont'd)

NO.	PROCESS DESCRIPTION
94.	Ethylene Oxide Via Oxidation of Ethylene (Air)
95.	Ethylene Oxide Via Oxidation of Ethylene (O_2)
96.	Ethylene Oxide Via Chlorohydration of Ethylene
97.	2-Ethylhexanol Via Oxo Process
98.	Formaldehyde Via Oxidation of Methanol
99.	Glycerine from Allyl Chloride
100.	Glycerine Via Epichlorohydrin
101.	Glycerine Via Allyl Alcohol and H_2O_2
102.	Hexamethylenediamine Via Acrylonitrile
103.	Hexamethylenediamine Via Adipic Acid
104.	Hexamethylenediamine Via Butadiene
105.	Hydrogen from Methane
106.	Hydrogen from Naphtha
107.	Hydrogen Via Partial Oxidation of Naphtha
108.	Hydrogen Cyanide Via Ammoxidation of Methane
109.	Hydrogen Peroxide Via Anthraquinone Process
110.	Hydrogen Peroxide from Isopropanol
111.	Isobutane Via Isomerization of n-Butane
112.	Isobutylene from Steam Cracked Butenes
113.	Iso-Octanol Via Heptenes (One-Step Oxonation)
114.	Iso-Octanol Via Heptenes (Two-Step Oxonation)
115.	Isophthalic Acid from m-Xylene
116.	Isoprene Via Dimerization of Propylene
117.	Isoprene Via Formaldehyde and Isobutylene
118.	Isoprene from C_5 Fractions
119.	Isopropanol Via Hydration of Propylene
120.	Isopropanol Via Propylene (Cation Exchange)
121.	Maleic Anhydride Via Oxidation of Benzene
122.	Maleic Anhydride Via Oxidation of n-Butane

TABLE 1. (Cont'd)

NO.	PROCESS DESCRIPTION
123.	Melamine Via BASF PROCESS
124.	Melamine Via CHEMIE LINZ Process
125.	Melamine Via NISSAN Process
126.	Melamine Via STAMICARBON Process
127.	Methanol from Methane
128.	Methanol Via Carbon Monoxide (High Pressure)
129.	Methanol Via Carbon Monoxide (Low Pressure)
130.	Methyl Acrylate Via Esterification of Acrylic Acid
131.	Methylene Diphenylene Diisocyanate Via Aniline and Phosgene
132.	Methyl Ethyl Ketone Via s-Butanol
133.	Methyl Ethyl Ketone from n-Butylenes
134.	Methyl Isobutyl Ketone Via Acetone
135.	Methyl Methacrylate Via Acetone Cyanohydrin
136.	Methyl Methacrylate from Isobutylene
137.	Nitric Acid (95%) Via Ammonia
138.	Nitric Acid (60%) Via Ammonia
139.	Nitrobenzene Via Nitration of Benzene
140.	Phenol Via Air Oxidation of Cumene
141.	Phenol Via Dehydrochlorination of Chlorobenzene
142.	Phenol Via Alkaline Hydrolysis of Chlorobenzene
143.	Phenol Via Sulfonation of Benzene
144.	Phosgene Via Carbon Monoxide and Chlorine
145.	Phthalic Anhydride from o-Xylene
146.	Phthalic Anhydride from Naphthalene
147.	Propylene, Chemical Grade from Propylene, Refinery
148.	Propylene, Poly. Grade from Propylene, Refinery
149.	Propylene, Poly. Grade Via Propylene, Chem. Grade
150.	Propylene Glycol Via Hydration of Propylene Oxide
151.	Propylene Oxide Via Chlorohydration of Propylene
152.	Propylene Oxide Via Oxidation of Propylene

TABLE 1. (Cont'd)

NO.	PROCESS DESCRIPTION
153.	Styrene Via Ethylene (Dehydrogenation)
154.	Styrene Via Ethylbenzene (Hydroperoxide Process)
155.	Sulfuric Acid Via Double Absorption Process
156.	Synthesis Gas (H_2:CO=1:1) Via Methane Reforming
157.	Synthesis Gas (H_2:CO=1:1) from Residual Oil
158.	Synthesis Gas (H_2:CO=2:1) Via Coal Gasification
159.	Synthesis Gas (H_2:CO=2:1) from Naphtha
160.	Synthesis Gas (H_2:CO=2:1) from Residual Oil
161.	Synthesis Gas (H_2:CO=3:1) Via Coal Gasification
162.	Synthesis Gas (H_2:CO=3:1) from Residual Oil
163.	Synthesis Gas (H_2:CO=3:1) Via Methane Reforming
164.	Terephthalic Acid, Fiber Grade Via p-Xylene
165.	Terephthalic Acid, Fiber Grade Via Crude TPA
166.	Terephthalic Acid, Crude Grade Via p-Xylene
167.	Terephthalic Acid, Crude Grade Via Acetaldehyde
168.	Toluene Diamine Via Dinitrotoluene
169.	Toluene Diisocyanate Via Toluene Diamine
170.	Urea Via Ammonia and Carbon Dioxide
171.	Urea Via Total Recycle Process
172.	Vinyl Acetate Via Ethylene and Acetic Acid
173.	Vinyl Acetate Via Acetylene and Acetic Acid
174.	Vinyl Acetate Via Ethane and Acetic Acid
175.	Vinyl Chloride from Ethylene
176.	Vinyl Chloride Via Ethylene Dichloride
177.	Vinyl Chloride Via Acetylene
178.	Vinylidene Chloride Via Dehydrochlorination of 1,1,2-Trichloroethane
179.	Vinylidene Chloride Via Vinyl Chloride
180.	Vinylidene Chloride Via Ethane Chlorination
181.	p-Xylene Via Isomerization of m-Xylene (Aromax-Isolene)
182.	p-Xylene Via Isomerization of m-Xylene (Parex-Isomar)

TABLE 2. LINEAR PROGRAMMING OPTIMAL SOLUTION. LIST OF CHEMICALS TO BE PRODUCED IN MEXICO

Chemical	Process[a]	Production, KT	Process Capacity, KT	%Capacity Utilization[b]
Acetaldehyde	1	2.4	136	2*
Acetic Anhydride	2	6.3	136	5*
Acrylic Acid	2	6.5	45	14*
Acrylamide	1	1.7	14	12*
Acrylonitrile	1	173	181	96
Acetylene	1	1.2	136	1*
Adipic Acid	1	6	136	4*
Aniline	1	16.8	45	37+
Benzene	1	297	90	
Bisphenol-A	1	5.6	45	12*
Cyclohexane	1	8.2	100	8*
Chlorobenzene	2	8.9	55	16*
Carbon Monoxide	2	50.7	159	32+
Dimethyl Terephtalate	2	215	150	
Dinitrotoluene	1	25.2	55	46+
Ethyl Acrylate	3	13.1	23	57*
Ethyl Benzene	1	271	522	52+
Ethylene Dichloride	2	289	272	
Ethylene Glycol	2	160	181	88
2-Ethylhexanol	1	51.4	64	80+
Ethylene Oxide	2	55.1	136	40+
Isobutylene	1	37.9	80	47+
Isopropanol	1	10.1	272	4*
Methyl Acrylate	1	7.4	45	16*
Methyl Ethyl Ketone	2	86	45	
Methanol	1	161	318	51+
MDI	1	11.1	45	25+
Methyl Isobutyl Ketone	1	19.5	23	85+
Maleic Anhydride	2	11	27	40+
Methyl Methacrylate	2	33.8	45	75+
Nitrobenzene	1	22.5	68	33+
n-Butanol	2	11	68	16*
Nitric Acid, 95%	1	500	66	
Nitric Acid, 60%	1	22	181	12*
Phtalic Anhydride	2	60.5	32	
Phenol	1	36	91	39+
Phosgene	1	34.5	61	57+
Propylene, polymer grade	2	267	181	
Propylene Glycol	1	15	45	33+
p-Xylene	2	205	91	
Styrene	1	89	454	20+
	2	148	454	33+
Sulfuric Acid	1	28.6	306	9*
Toluene Diamine	1	15.2	36	42+
Toluene Diisocianate	1	20	45	44+
Terephtalic Acid, crude	1	301	181	
Terephtalic Acid, fiber grade	2	170	181	94
Urea	1	2103	340	
Vinyl Acetate	2	50	136	37+

Table 2. (continued)

Chemical	Process[a]	Production, KT	Process Capacity, KT	%Capacity Utilization[b]
Vinyl Chloride	2	168	181	93
	3	174	272	64+
Vinylidene Chloride	1	3.3	23	14*

[a]Process numbers refer to Table 1.

[b]Given only for processes whose value is lower than 100%

*Capacity utilization is lower than 20%, therefore these processes are not recommended.

+Processes subject to further analysis

c) 21 processes have a utilization factory between 20 and 79%; they will be subject to more detailed analysis using MIP. A binary variable will be defined for each of these processes to determine if they are really economical.

Notice that we have used a heuristic rule by classifying the processes in this manner to reduce our search space when applying MIP. However, the approach tends to be conservative since processes with 30% utilization factor, for instance, are unlikely to be economically practical.

This MIP version of the problem was run using the FMPS-MIP routine (12) of the Univac 1110. An optimal solution was obtained after 41.5 seconds of CPU time, with an objective function value of 4.323×10^9 \$/year (4.8% higher than the LP model). The results show significant differences with respect to the LP solution. Only 3 out of the 21 processes defined via binary variables were accepted by the model: one to produce methanol from methane, another to produce methyl methacrylate from isobutylene, and the third to manufacture vinyl chloride. Table 3 reports the chemicals whose production is economically attactive. Some observations on this solution and its differences with respect to the LP solution are given below.

a) Since a fixed investment ought to be made for a methanol plant, the MIP model looked for additional market for this chemical in order to achieve better economies-of-scale. Thus, 34.5 KT of formaldehyde were now produced, making use of 156 KT of methanol. This created a total demand for the latter of 317 KT, which drives the plant to operate at almost full capacity (318 KT).

TABLE 3. MIXED-INTEGER PROGRAMMING OPTIMAL SOLUTION. LIST OF CHEMICALS TO BE PRODUCED IN MEXICO

Chemical	Process[a]	Production,KT	LP Solution	Process Capacity,KT	%Capacity Utilization[b]
Acrylonitrile	1	171	(173)	181	94
Benzene	1	69.2	(297)	90	77
Dimethyl Terephtalate	2	215	(215)	150	72 (2)
Ethylene Dichloride	2	272	(289)	272	100
Ethylene Glycol	2	160	(160)	181	88
2-Ethylhexanol	1	51.4	(51.4)	64	80
Formaldehyde	1	134.5	(0)	45	99 (3)
Methanol	1	317.1	(161)	318	99*
Methyl Isobutyl Ketone	1	19.5	(19.5)	23	85
Methyl Methacrylate	2	33.8	(33.8)	45	75*
Nitric Acid	1	487	(500)	66	92 (8)
Phtalic Anhydride	2	60.5	(60.5)	32	95 (2)
p-Xylene	2	89.7	(205)	91	99
Terephtalic Acid crude	1	131.9	(301)	181	73
Terephtalic Acid fiber grade	2	170	(170)	181	94
Urea	2	2091	(2103)	340	88 (7)
Vinyl Chloride	2	159.3	(168)	181	88
	3	182.7	(174)	272	67*

[a]Process numbers refer to Table 1.

[b]Number of Plants given when more than one is needed.

*Processes selected via MIP model.

b) A process to produce ethylbenzene and four other technologies that made use of benzene were not selected. This lessened the production of benzene to its exogenous demand of 69.2 KT.

c) 236.6 KT of terephtalic acid crude (TPAC) are shown to be more economic as imports; this dwindles the operation of TPAC process from 301 KT (LP solution) to 131 KT, which in turn lowers the internal need for p-xylene by 119 KT and methyl ethyl ketone by 42 KT. TPAC is then used in the manufacture of terephtalic acid fiber grade and in the production of dimethyl terephtalate.

d) The demand for vinyl chloride (VCM) is met by two different processes: VCM via dehydrochlorination of ethylene dichloride and VCM via hydrochlorination of acetylene. 289 KT of ethylene dichloride are produced via oxychlorination of ethylene, which also meet the exogenous demand for that chemical.

e) A total investment of $1.69 billion is required to build this industry.

Notice that the 3 processes selected correspond to those with the highest capacity utilization of the 21 considered. Processes with a utilization factor lower than 60% were not chosen by the model.

The economic model used in this study shows also some differences with respect to the LP model of the Mexican petrochemical industry developed by Trevino (3,5), where an objective function in terms of carbon-content units was used. In Trevino's work, it was shown that ethylene and VCM should be imported, contrary to the Mexican practice of building large plants to produce these chemicals. In the present study

we have found that, while ethylene should actually be imported, VCM should be produced by the technologies mentioned above. Moreover, the high demand for ethylene seems to make its domestic production advisable, since the import cost used in the model for this chemical appears to be too low. Better projections of import costs can be obtained by extending the study presented by Fathi-Afshar and Rudd (13). By using an integrated model of the U.S. petrochemical industry, they found that the dual variables associated with the optimal solution give a good estimation of the prices of chemicals. These values can then be used as import costs in our Mexican model.

Near-optimal solutions

In addition to the optimal solution, some near-optimal structures of the Mexican petrochemical industry were detected in the MIP run. The best is reported in Table 4. Its objective function value is 4.3244×10^9 \$/year, only 0.01% higher than the optimal solution. There are three main differences between this solution and the optimal solution:

a) Ethyl acrylate is produced from acetylene in an amount of 13.13 KT, 57% of the process capacity. This is the process that makes the lowest use of its capacity of those selected in this solution.

b) Methanol is not produced, which causes a switch in the method used for benzene production. A process via disproportionation of toluene is used instead of hydrodealkylation of toluene. The latter provided some of the methane that was required to produce methanol. As this chemical is no longer produced, methane finds no utilization in the network, and a switch occurs to a technology

TABLE 4. MIP NEAR-OPTIMAL SOLUTIONS

Chemical	Process[a]	Production,KT	Process Capacity,KT	%Capacity Utilization
Acrylonitrile	1	171	181	94
Benzene	2	69.2	90	77
Dimethyl Terephtalate	2	215	150	72 (2)
Ethyl Acrylate[b]	3	13.13	23	57
Ethylene Dichloride	2	272	272	100
Ethylene Glycol	2	160	181	88
2-Ethylhexanol	1	51.4	64	80
Methyl Isobutyl Ketone	1	19.5	23	85
Methyl Methacrylate	2	33.8	45	75
Nitric Acid	1	487	66	92 (8)
Phtalic Anhydride	2	60.5	32	95 (2)
p-Xylene	2	89.7	91	99
Terephtalic Acid crude	1	131.9	181	73
Terephtalic Acid fiber grade	2	170	181	94
Urea	1	2091	340	88 (7)
Vinyl Chloride	2	159.3	181	88
	3	182.7	272	67

[a]Process numbers refer to Table 1.

[b]This process is not selected in the second near-optimal solution.

where a more valuable byproduct is obtained. Thus, xylenes are coproduced in the benzene process, and are then used in the manufacture of p-xylene.

c) The investment requirements for this alternative are \$1.57 billion, as opposed to \$1.69 billion in the optimal solution.

A second near-optimal solution, with an objective value of 4.3248×10^9 \$/year (0.025% higher than the optimal case), was also detected. The structure is very similar to the one just described. It differs in the deletion of the ethyl acrylate process, which has a very low economic impact on the industry. A total investment of \$1.55 billion is required.

The model has thus generated three alternatives that, for practical purposes, seem equally attractive. Subsequent expansions of the petrochemical industry can be simulated by taking the processes selected in this solution as lower bounds, and using 0-1 decision variables for the processes included in the model again. This would permit an orderly growth of the industry by doing a proper substitution for imports at the right time. The use of alternate plant sizes can also be considered.

A heuristic method via linear programming

The MIP model provided an optimal solution which turned out to be very different from that obtained by the LP formulation. In this section, it is shown how linear programming can be recursively used to get a near-optimal, if not optimal solution. The method consists of a parametric study involving the capacity utilization factor and a modified objective function. Taking the solution of the initial LP relaxation reported in

Table 1, we can develop the following approach. Let α be the minimum utilization factor for a process to be selected. Initially, only processes with $\alpha = 20\%$ will be considered within the feasible set of the LP problem; then, this minimum is increased to 30% and so on. As α increases, the total cost of energy and materials goes up, but the investment requirements should decrease, and an optimal compromise should be expected. On formulating the objective function, one can think of the fixed investment term as being a constant, that can be added to the objective value after the LP technique has been applied. The objective function can be written as:

$$\min \quad Z^{LP} = \sum_{i=1}^{N} F_i P_i + \sum_{j \in M'} C_j^* X_j + \sum_{i=1}^{N} I_i B_i$$

where M' is the set of processes with an acceptable utilization factor; all other terms have been previously defined. This objective is then corrected by adding the fixed investment term of the processes selected, that is,

$$Z^* = Z^{LP} + \sum_{j \in S} E_j^*$$

where S is the set of opened plants. The strategy of the method is given in Figure 4.

The behavior of the objective function for a utilization factor α between 20 and 80% is displayed in Figure 5. The function exhibits a minimum when $\alpha = 60\%$, so that only processes operating at least at 60% of their nominal capacity should be installed in the country. This

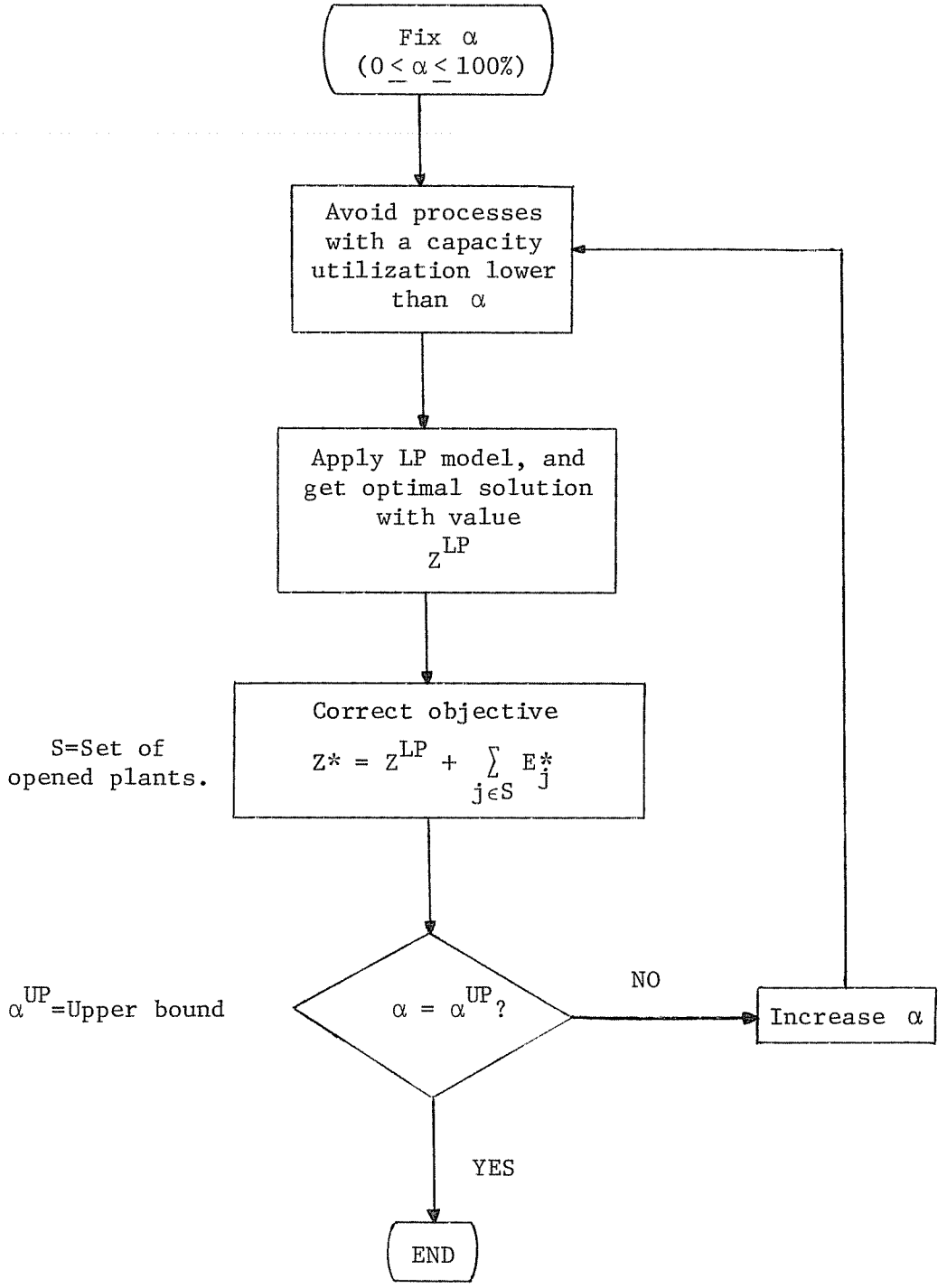


Figure 4. Strategy of the heuristic method.

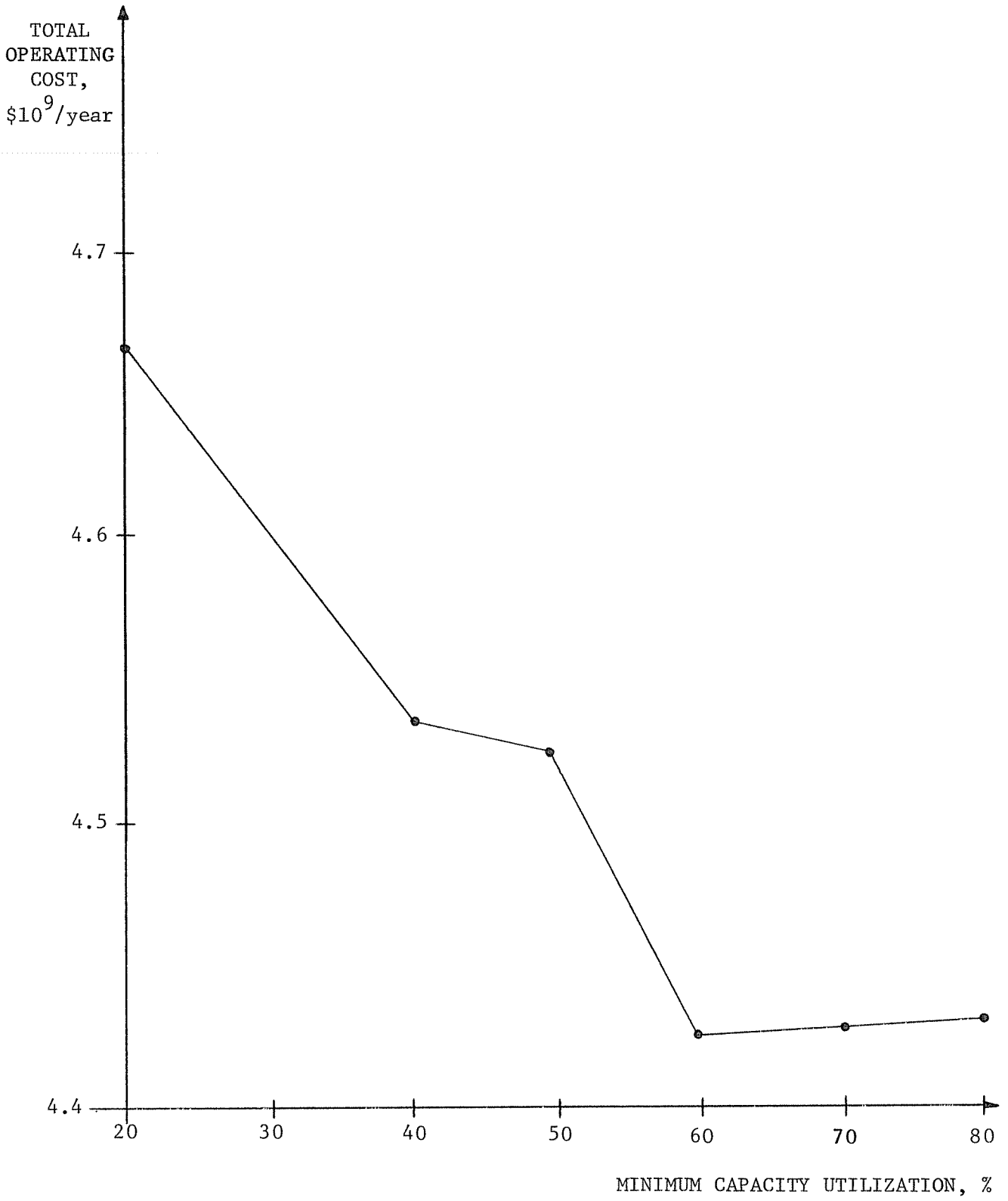


Figure 5. Results obtained by the heuristic method.

cut agrees with that observed in the MIP model. The correct objective value turns out to be 4.426×10^9 \$/year, 2.37% higher than the MIP model. The processes selected in this solution are reported in Table 6. There are 16 chemicals produced. Some differences with respect to the MIP solution are observed:

a) Processes to produce methyl ethyl ketone and propylene polymer grade are selected.

b) Ethylene glycol, formaldehyde and methanol are imported.

c) Benzene is produced via disproportionation of toluene because of the coproduction of acetylene, as observed in the near-optimal MIP solutions.

d) Terephtalic acid fiber grade is produced from acetic acid and p-xylene instead of using terephtalic acid crude grade. The new technology, although more expensive, makes a more efficient use of feedstocks and energy. As the investment term has been taken out of the objective function, the latter factor becomes dominant and a new technology is chosen. The total need for p-xylene increases to 242 KT, and this chemical is produced via isomerization of m-xylene.

The structure of the industry for a α equal to 70 and 80 percent is also given in Table 6. The deletion of processes to manufacture benzene, methyl methacrylate and acetylene-based vinyl chloride has a minor economic impact on the system. Benzene and methyl methacrylate are imported, whereas vinyl chloride production via ethylene dichloride is increased, yielding overall savings on investment of \$90 million.

TABLE 5. OPTIMAL VALUES GENERATED FOR α = 20% - 80%

α	Z*
20	4.668×10^9
40	4.537
50	4.526
60	4.426
70	4.429
80	4.431

TABLE 6. PROCESSES SELECTED IN THE PARAMETRIC STUDY FOR FOUR VALUES OF THE MINIMUM CAPACITY UTILIZATION FACTOR

Chemical	Process[a]	Production, KT α=50%	α=60%	α=70%	α=80%
Acrylonitrile	1	171	171	171	171
Benzene	1	74	0	0	0
	2	194.6	69.2	69.2	0
Dimethyl Terephtalate	2	215	215	215	215
Ethyl Acrylate	3	13.13	0	0	0
Ethyl Benzene	1	270	0	0	0
Ethylene Dichloride	2	289	289	575	575
2-Ethylhexanol	1	51.4	51.4	51.4	51.4
Methyl Ethyl Ketone	2	59	59	59	59
Methanol	1	158.4	0	0	0
Methyl Isobutyl Ketone	1	19.5	19.5	19.5	19.5
Methyl Methacrylate	2	33.8	33.8	33.8	0
Nitric Acid	1	487	487	487	487
Phtalic Anhydride	1	60.5	60.5	60.5	60.5
Propylene, polymer grade	2	267	267	267	267
p-Xylene	1	242	242	242	242
Styrene	2	237	0	0	0
Terephtalic Acid, crude	1	189	189	189	189
Terephtalic Acid, fiber grade	1	170	170	170	170
Urea	1	2091	2091	2091	2091
Vinyl Chloride	2	170	170	342	342
	3	172	172	0	0
Total Operating Cost, 10^9/year		4.526	4.426	4.429	4.431
Investment requirements, 10^9		2.34	1.90	1.88	1.81

[a] Process numbers refer to Table 1.

Again, several alternatives with similar operating cost were detected. Some other factors like less dependence on foreign supply of chemicals, which would promote more investment, should be taken into account in a decision-making process. However, most developing countries face a situation where capital available for investment is scarce, and a suitable allocation of it is imperative. In these cases, the kind of information developed in this study is of special value.

Another heuristic approach using a unit investment term in the objective function has been developed (14). After applying the LP algorithm, the result was corrected for the error shown in Figure 1. An optimum solution was again observed when $\alpha = 60\%$, and the objective value obtained was only 0.16% higher than the MIP model. These results suggest further research comparing these heuristic methods.

Conclusions

Mixed-Integer Programming has proved to be a useful tool for the selection of chemical processes. Grossman and Santibanez (15) illustrated the use of MIP in the synthesis of a chemical complex.

In this work, an approach for the development of a Mexican petrochemical industry using MIP is proposed. Plants of optimal size for the U.S. were used in this analysis, and only 18 technologies seemed appropriate for Mexico under the economic environment considered here. In this sense, LP solutions can be misleading since 52 technolgies were selected by using such a technique, and 34 of those were shown not to be economical. This also demonstrates the important role that economies-of-scale play in the economics of a chemical process. Two additional solutions with objective values within 0.025% of the optimal were also detected using MIP.

A heuristic approach using a parametric study on capacity utilization via linear programming was also presented. The method provided a solution with an objective function only 2.3% higher than the MIP model. Some near-optimal structures were also detected by means of the approach.

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