SYSTEMS STUDY OF THE PETROCHEMICAL INDUSTRY

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ABSTRACT

The modern petrochemical industry is the result of the action over decades of incompletely understood economic, technical, and political forces. It is to be hoped that this complex industrial system has evolved into an efficient and flexible provider of the needs of the economy. We seek to determine the strengths and weaknesses of the industry and to perceive opportunities for further development. A systems model of the industry provides the necessary insight.

A criterion of efficient feedstock utilization on the model of the industry reproduces the dominant structure of the actual industry, thereby lending credence to the model and the performance criterion. Fourteen of the twenty chemicals for which the current production practices differ from those proposed by the model are the subject of current development interest. The remaining six chemicals are produced in the model by currently obsolete processes that may be revived. The response of the verified model to scenerios of potential future developments provides points of departure for planning the long-range development of the industry.

INTRODUCTION

The petrochemical industry is a complex economic system. Over 3,000 petrochemicals are made commercially, nearly 400 major companies are engaged in some segment of the processing, and there are 50 separate organizations among the two leading producers of each of the top 100 petrochemicals. The hundreds of segments of this system interact by competing for raw materials and markets, and by developing and licensing competing process technologies. Thus, if particular segments of the industry are examined in isolation, there is no guarantee that the conclusions reached will be significant when the performance of the overall system is of importance. In such a large, interactive system, the whole is not necessarily made more efficient if one particular part is improved. In fact, local inefficiencies may be necessary if the overall system is to operate at maximum efficiency. Consequently, in this study of the petrochemical industry, we concentrate not on the local economics of individual segments of the industry, but on the performance of the system as a whole. For this purpose a mathematical model of the system is constructed.

Because of the size and complexity of the petrochemical industry, it is not practical to consider the fine details of its interactive corporate structure when constructing a model of the overall system. Instead we look past the system's organizational structure and model the system by taking advantage of its underlying stoichiometric framework. Accordingly, the petrochemical industry is regarded as a system of chemical reactions which convert crude petrochemical feedstocks into the products consumed by the economy. In this way the system can be described using the stoichiometric and yield data characterizing each chemical transformation. These data are generally available in the literature and are the basis for the model described below.

Though this model may overlook locally important technological and economic factors, it effectively approximates the gross behavior of the industry. To study the efficiency with which the petrochemical industry consumes feedstocks, we use the model to determine technological bounds on the structure of the industry and on the performance of its parts. These results are based on the criterion that the industry as a whole meet the demands of the economy with minimum feedstock consumption and unconstrained by the limits of existing process capacity. The model is also used to study the effects of certain perturbations in present patterns of feedstock supply and product demand. This represents one part of a larger study of the industry [1,2].

NATURE OF THE INDUSTRY

The basic feedstocks for the petrochemical industry are extracted from natural gas or are produced as byproducts of petroleum refining. Coal has largely been replaced as a feedstock source, but may increase in significance in the face of predicted natural gas and petroleum shortages. The petrochemical industry converts its primary feedstocks into a variety of final and intermediate chemical products. The intermediates are consumed within the industry itself; the final products are used elsewhere in the economy, primarily as raw materials for other goods, such as plastics, elastomers, and synthetic fibers. Because its products are raw materials for many downstream industries, the petrochemical industry is a particularly important link in our economic system.

For the manufacture of a given chemical there are often two or more chemical transformations available, each involving different combinations of feedstocks and coproducts. For example, there are three chemical reactions that have been used commercially to manufacture acrylonitrile: the reaction of acetylene and hydrogen cyanide, the reaction of ethylene oxide and hydrogen cyanide, and the reaction of propylene, ammonia, and air. Some petrochemicals, including ethylene, butadiene, phenol, and acrylic acid can be produced from as many as five different combinations of feedstocks.

Radically different methods of executing a given chemical transformation are not as commonly found, however. The freedom with which chemical processing know-how is licensed world-wide enables all manufacturers to acquire the superior processing methods. Thus, the differences within the industry tend to be dominated by discrete and drastic differences in the feedstocks used, while the technology used to implement a particular reaction route is relatively uniform. Furthermore, the kind of process technology used to produce the majority of petrochemicals is similar in sophistication and capital intensiveness. One sector of the industry does not differ greatly from any other in the level of technical competence required. Finally, for most petrochemicals, feedstock costs

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dominate the economics of production, typically representing 45 to 80 percent of the production cost. This fact, along with the observations made above on the uniformity of process technology, suggests that it is the flexibility with respect to feedstocks and coproducts which dominates the behavior of the petrochemical industry. The details of a particular processing method may alter local economics to some extent, but the prevailing industrial structure is determined by the more primitive forces that control the gross production and consumption of materials.

In summary, the petrochemical industry is bounded on one side by sources of primary chemicals derived from crude oil, natural gas, and coal, and is bounded on the other side by the consumer market that requires synthetic materials of great diversity. Within these boundaries the industry is a flexible, interdependent system of commercially proven chemical transformations, the execution of which does not differ greatly around the world. However, the cast of chemical transformations used can vary widely in both time and location to meet the needs of an economy. In any case, it is the gross production and consumption of materials that is of primary importance.

Given these conjectures on the nature of the petrochemical industry, we construct a model which effectively accounts for its flexibility and interdependence, and which can be used to study the efficiency with which it produces and consumes materials. The model is verified by its ability to predict the current industry. This model is described mathematically in the next section.

MATHEMATICAL FORMULATION OF MODEL

We view the petrochemical industry as a system of M chemical transformations that produce or consume N chemicals. To be general, assume that each of the N chemicals is potentially a primary input or final product of the industry. Let p_i be the amount of chemical i used as a primary feedstock; let q_i be the amount of chemical i emerging as a final product; and let x_j be the amount of transformation j used by the industry.

If chemical i is produced by transformation j, let a_{ij} be the amount of i produced per unit of j; if i is consumed by j, let $-a_{ij}$ be the amount of i consumed per unit of j; if i is neither an input or output of j, let $a_{ij} = 0$. The a_{ij} are known as 'input-output coefficients', and $\underline{\underline{A}} = [a_{ij}]$ is called the 'technology matrix'.

In these terms, material balances can be written for each chemical as

$$p_i + \sum_{j=1}^{M} a_{ij}x_j - q_i = 0, \quad i = 1,2, \ldots, N ; \tag{1}$$

or in matrix form

$$\underset{\sim}{p} + \underline{\underline{A}}\underset{\sim}{x} - \underset{\sim}{q} = \underset{\sim}{0} \; , \qquad (1a)$$

where $\underset{\sim}{p} = (p_i)$, $\underset{\sim}{q} = (q_i)$, and $\underset{\sim}{x} = (x_j)$.

In the short-range Eq. (1) is constrained by the supply of feedstocks,

$$\underset{\sim}{p} \leq \underset{\sim}{s} \; , \qquad (2)$$

by the demand for products,

$$\underset{\sim}{q} \geq \underset{\sim}{d} \; , \qquad (3)$$

and by the capacity for each chemical transformation,

$$\underset{\sim}{x} \leq \underset{\sim}{c} \; , \qquad (4)$$

where $s = (s_i)$ and $d = (d_i)$ are supply and demand data which might be assembled by functional aggregate studies [1,2], and $c = (c_j)$ represents industrial capacity.

Equations (1)-(4) form a linear system of constraints within which the industry must function in the short-range. These constraints, together with a linear objective function, form a linear programming problem which can easily be solved to determine the p_i, q_i, and x_j satisfying the given objective.

CONSTRUCTION OF MODEL

The first step in constructing the model formulated above is the selection of the chemicals and chemical transformations which constitute the model.

A list of the chemicals chosen appears in Table 1. The selection is based on volume of production; in general, petrochemicals for which production exceeded 100 million pounds in the United States in 1970 are included, together with the primary feedstocks, organic and inorganic, which may be involved in their production. Chemicals produced in lesser quantities are included if they are potentially an intermediate, coproduct, or major byproduct in the manufacture of one of the larger volume chemicals selected. However, intermediate chemicals which have essentially only one use and for which there is essentially only one manufacturing route are not included explicitly, unless there is significant commercial traffic in that chemical (as in the case of cumene or ethylbenzene, for example). Table 1 also indicates the function of each chemical selected; that is, whether it serves as a primary input, final output, intermediate, or combination of the above.

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For each chemical selected, the model includes the chemical transformations currently used to manufacture the chemical, as well as any now obsolete transformations once used on a commercial scale. By accounting for obsolete in addition to current process technology we assure that the model is not biased toward any particular economic environment and can adapt to radically different patterns of supply and demand. Once obsolete processes could conceivably return to prominence if the appropriate economic environment evolved. Table 2 lists the chemical transformations accounted for by the model. The model has been expanded since this work to include 250 transformations.

The heart of the model is the technology matrix. Hence the estimation of the input-output coefficients is a key step in constructing the model. For this purpose yield data for each chemical transformation is required.

Most of the yield data used is taken from the Stanford Research Institute publication, *Chemical Conversion Factors and Yields* [3]. Most of the yield data reported in this volume was obtained directly from the industry, or was at least subject to industry review. Thus, data from this source can be considered reasonably reliable. The remainder of the yield data used is drawn primarily from surveys of the industry by Brownstein [4], Hahn [5], Goldstein and Waddams [6], and Faith, Keyes, and Clark [7]. Various articles in the trade journals have also been consulted, but some of the data reported in these articles is drawn from the patent literature and so must be regarded with some skepticism. The estimated values of the input-output coefficients and a complete listing of data sources will appear elsewhere [8].

Needed to complete the construction of the model are supply, demand, and capacity data. Since the industry must compete for its feedstocks and markets, supply and demand data are best determined by functional aggregate studies [1,2]. Here, however, supply and demand are estimated using observed values of production and observed usage patterns. Production data is taken primarily from U.S. Tariff Commission and U.S. Bureau of Mines reports [9,10]. Usage patterns for most of the chemicals of interest are compiled by Brownstein [4] and Waddams [11]. The studies described below are based on estimated patterns of supply and demand in the United States in 1970. This data and a complete listing of sources will appear elsewhere [8]. Capacity data is not required for the studies described below and so its collection is not considered here.

EFFICIENT FEEDSTOCK UTILIZATION

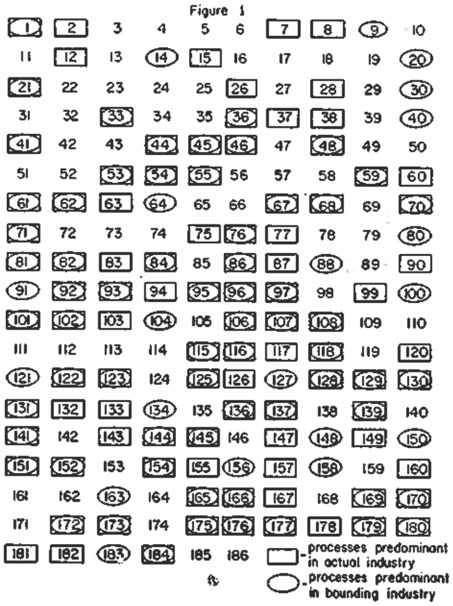
In this section we use the model described above to study the efficiency with which the industry consumes feedstocks. We seek to establish a bound on the structure of the industry, and this bound is to satisfy the criterion that feedstock consumption is minimized. In addition, we look for bounds on the efficiency of feedstock consumption by the various parts of the industry.

Since carbon atoms form the backbone for most petrochemical molecules, we choose to measure feedstock in terms of carbon content. Thus, if $\omega_{C,i}$ is the weight fraction carbon in feedstock i, the problem is to find the p_i, q_i, and x_j which minimize $\sum_i \omega_{C,i} p_i$, and which satisfy

Eqs. (1)-(3). This represents an optimization problem which is easily solved using linear programming. Note that the capacity constraint, Eq. (4), is not used, since this would impose the current industrial structure on the solution. By relaxing the capacity constraint a bound independent of any particular economic setting can be obtained. This bound thus represents the ultimate performance of the industry with respect to feedstock consumption. Also note that the consumption of carbon to provide process energy is not considered in the objective function, since most of the fuel used by the industry is for the generation of steam or electricity [12], and thus in the long-range is not necessarily tied to feedstock carbon.

The structure of the bounding industry found by solving the linear programming problem given above is compared with the predominant structure of the actual industry in Fig. 1. Each number in Fig. 1 represents a commercially proven process technology listed in Table 2. The current technology and that predicted by the model are marked to identify the technology that is common and that which differs. It is evident from Fig. 1 that much of the dominant structure of the industry is predictable.

Figure 1. A comparison of the processes predominant in the actual industry in 1970 and processes predominant in the bounding industry. Each number corresponds to a process listed in Table 2.



For fourteen of the twenty chemicals for which the actual and bounding industries differ, the processes used by the bounding industry are the subject of current interest and could someday come to predominate. For example, the production of acetic acid from methanol is already nearing predominance. Only in the manufacture of six chemicals, acetone, ethylene oxide, phenol, ethyl acetate, acetic anhydride, and vinyl acetate does the bounding industry use obsolete processes. In the case of ethylene oxide, the bounding industry prefers the chlorohydrin process to the direct oxidation of ethylene. This is not surprising since the chlorohydrin process offers a much higher yield. However, this is offset by the need to consume chlorine, which was not accounted for in finding the bounding industry. In the case of phenol, the bounding industry prefers the chlorobenzene route to the cumene route. The yield of phenol from chlorobenzene is higher than from cumene, but in practice this is offset by the coproduction of acetone when cumene is used. In the bounding industry, however, acetone is produced from acetic acid, which is very efficiently produced from methanol and synthesis gas. Thus, there is no need for the coproduct acetone and the cumene route is rejected. Similar arguments explain the use in the bounding industry of the other obsolete processes.

The bounding industry and the actual industry are strikingly similar. This leads us to two important conclusions. First, it indicates that the petrochemical industry in its current form is a quite efficient user of its feedstocks, and in fact approaches rather closely the configuration in which feedstock consumption is minimized. Second, it implies that an underlying driving force in the development of the petrochemical industry has been the minimization of feedstock consumption. This is particularly interesting because it suggests that industrial planning can be based, at least in its preliminary stages, on studies of raw material consumption using simple technological models of the type described above.

Associated with each constraint in a linear programming problem is a dual variable, or 'shadow price', which is essentially the partial derivative of the objective function with respect to the right-hand-side coefficient of the constraint. Thus, in the linear programming problem being considered here, the shadow prices associated with Eq. (3) represent the marginal increase in overall feedstock consumption as the demand for a given chemical increases. By comparing the shadow prices with theoretical feedstock requirements one can determine the efficiency with which individual chemicals are produced. The theoretical carbon requirement for the manufacture of a given chemical is simply its weight fraction carbon. We define the ratio of the theoretical carbon requirement for a chemical to its shadow price as its 'feedstock efficiency index'. This represents a measure of the ultimate performance of each part of the industry when totally integrated.

Table 3 lists, for the bounding industry, the feedstock efficiency indices of 25 selected chemicals. Note that a chemical's feedstock efficiency index may exceed unity if it can be manufactured from byproducts of other processes. For example, in the bounding industry acetic acid is derived from carbon monoxide, which is contained in or can be manufactured from the off-gases from various processes. The feedstock efficiency indices provide insight into the strengths and weaknesses of the industry and suggest areas in which further development is possible. Thus, they may be useful parameters in a dynamic model of the industry such as that proposed by Rudd [1,2], in which the impact of new technological developments is considered.

PERTURBATIONS IN SUPPLY AND DEMAND

In this section we use the model to study the effects of perturbations in present patterns of supply and demand. As shown above, the actual structure of the industry is approximated by the structure of the bounding industry that minimizes feedstock consumption. Thus, by using the model to determine the effect of perturbations on the bounding industry, it is possible to gain some insight into what may occur within the actual industry when so perturbed. Such insight provides a point of departure for long-range planning by the industry.

Essentially all of the industry's primary feedstocks are now derived from petroleum and natural gas. However, the possibility of natural gas shortages may cause the industry to turn away from natural gas as a feedstock supplier. For instance, it has been predicted for several years that liquid petroleum fractions such as naphtha or gas oil would replace feedstocks derived from natural gas in the production of ethylene and other chemicals. Another more recent suggestion is that synthesis gas and methane produced from coal would replace natural-gas-derived feedstocks in some applications. We use the model to consider these two scenarios.

Consider a scenario in which natural gas is completely eliminated as a feedstock source and an unlimited supply of naphtha and gas oil is available as a replacement. When the supply constraints are perturbed accordingly, changes are observed in the structure of the bounding industry, as shown in Fig. 2. The resultant changes in the feedstock efficiency indices are indicated in Table 3.

Figure 2. A comparison of the bounding industry and the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and naphtha and gas oil are made available as a replacement. Each number corresponds to a process listed in Table 2.

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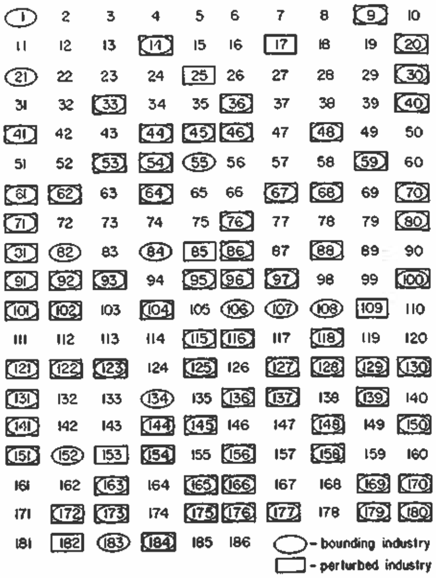

The most important structural change shown in Fig. 2 is the switch to naphtha as the feedstock for ethylene manufacture. Other structural changes can be interpreted in terms of the increased production of byproducts, such as propylene, butadiene, isobutylene, and isoprene, which results when ethylene is produced from naphtha. For example, processes using propylene to produce acetone and cresylic acid, and a process using isobutylene to produce methyl methacrylate enter the perturbed industry. Both isobutylene and isoprene are produced in surplus; nearly 90% of the acetylene, nearly 60% of the butadiene, and essentially all of the methane are produced as byproducts of ethylene manufacture. The feedstock efficiency indices listed in Table 3 indicate that the naphtha-based industry is somewhat less efficient in terms of carbon consumption than the natural-gas-based industry, although some chemicals produced from ethylene byproducts can be manufactured with less feedstock consumption.

Consider next a scenario in which natural gas is completely eliminated as a feedstock source and an unlimited supply of coal-derived methane, hydrogen, and carbon monoxide is available as a replacement. The structural changes observed when the industry is so perturbed are shown in Fig. 3. The feedstock efficiency indices for the perturbed industry are shown in Table 3.

The most significant structural change indicated in Fig. 3 is the increased use of acetylene, which is used to produce all the vinyl chloride and trichloroethylene and nearly half the ethylene. Although the supply of carbon monoxide to the perturbed industry is unbounded, all of the carbon monoxide used is produced as a byproduct of the manufacture of acetylene from methane using the partial oxidation process. The feedstock efficiency indices listed in Table 3 show that ethylene and its derivatives are manufactured quite inefficiently. This suggests the need for developing new process technology, in particular technology which would permit the conversion of synthesis gas directly to ethylene or ethanol. This has been accomplished in the laboratory, but there have been no commercial developments other than a small plant operated briefly in 1956

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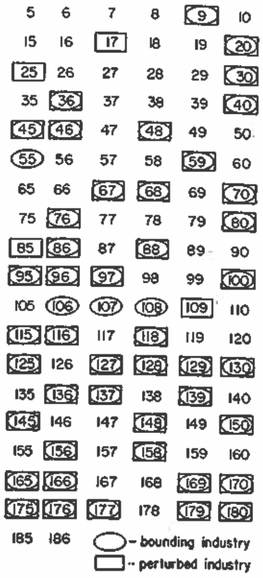

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which converted synthesis gas to ethanol and acetaldehyde [13]. Although this scenario and the one considered above are extreme cases, they serve to demonstrate the applicability of the model to problems of long-range industrial development.

Figure 3. A comparison of the bounding industry and the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and coal-derived methane and synthesis gas are made available as a replacement. Each number corresponds to a process listed in Table 2.

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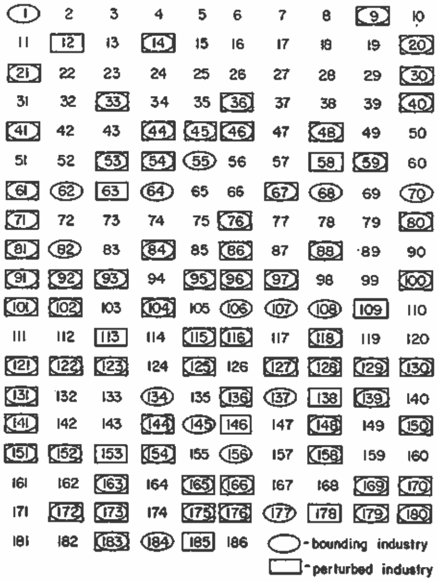

We now use the model to consider two perturbations in the present pattern of demand for petrochemicals: the reduction in demand for vinyl chloride due to restrictions on the use of polyvinyl chloride in food-related applications, and the reduction in demand for chlorofluoromethanes due to restrictions on its use as an aerosol propellant.

The discovery that vinyl chloride is a carcinogen has prompted the proposal of regulations which would ban the use of polyvinyl chloride (PVC) in food packages such as bottles and blister packages. It is not likely that PVC will be replaced in these applications by a single plastic; instead a variety of plastics, including polyethylene terephthalate, oriented polypropylene, polycarbonate, and acrylonitrile copolymers will compete to replace PVC. A number of scenarios were considered in which PVC was replaced by another plastic or combination of plastics. In each case no structural changes in the bounding industry were observed. This is not surprising since the use of PVC in the food packages affected by the proposed ban accounts for less than 1% of the total demand for vinyl chloride [14]. Even if PVC were banned from all food related use, including water pipes, the demand for vinyl chloride would be reduced by only about 15%. Perturbations of this magnitude still produce no structural changes in the bounding industry.

There is evidence suggesting that the release of chlorofluorocarbons into the atmosphere could be reducing the concentration of ozone in the stratosphere, thereby increasing the amount of ultraviolet radiation reaching the earth's surface. Since this would result in an increased incidence of skin cancer, there are proposals which would ban the use of chlorofluorocarbons in aerosol propellants. This application accounts for about 50% of the demand for chlorofluoromethanes. Possible replacements in aerosol formulations are n-butane, isobutane, and carbon dioxide. However, n-butane and isobutane are flammable and thus not suitable for household use, and carbon dioxide aerosols are subject to clogging. Thus, at least for the near future, it seems likely that if chlorofluoromethanes were banned, new propellants would be avoided entirely, and finger-powered spray pumps would be used. Imposing this perturbation on the bounding industry reveals no structural changes, but does show that nearly all the carbon tetrachloride required by the perturbed industry is produced as a byproduct of perchloroethylene manufacture.

CONCLUDING REMARKS

The model described here is essentially a static model of resource allocation. When considering the projection of industrial development the static model can be used with the criterion of minimum feedstock consumption to gain some insight into the future of the industry. However, it is likely that a dynamic model of the industry could provide sharper perception of future developments. The static model presented here represents one step toward the development of such a dynamic model [1,2].

The application of these concepts in planning the rapidly growing Mexican petrochemical industry will be reported soon [15], as will a comprehensive study of the entire problem of the long-range development of the industry [16].

ACKNOWLEDGEMENT

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Table 1. A list of the chemicals which constitute the model industry. Also indicated is the potential function of each chemical in the model industry: I = primary input, M = intermediate, O = final output.

Chemical	Function	Chemical	Function	Chemical	Function	Chemical	Function
Acetaldehyde	MO	Carbon Dioxide	MO	Fuel Oil	O	Nitrobenzene	MO
Acetic Acid	MO	Carbon Disulfide	MO	Fumaric Acid	O	Peracetic Acid	MO
Acetic Anhydride	MO	Carbon Monoxide	IMO	Gas Oil	I	Perchloroethylene	O
Acetone	MO	Carbon Tetrachloride	MO	Glycerine	O	Phenol	MO
Acetylene	MO	Chlorine	IM	Hexamethylenediamine	O	Phosgene	MO
Acrolein	MO	Chlorobenzene	MO	Hydrogen	IMO	Phthalic Anhydride	MO
Acrylic Acid	MO	Chloroform	O	Hydrogen Chloride	IMO	Propane	IMO
Acrylonitrile	MO	Chloroprene	O	Hydrogen Cyanide	MO	Propylene	IMO
Adipic Acid	MO	Cresylic Acid	O	Hydrogen Fluoride	I	Propylene Dichloride	MO
Adiponitrile	MO	Cumene	MO	Hydrogen Peroxide	I	Propylene Glycol	O
Allyl Alcohol	MO	Cyclohexane	MO	Isobutane	I	Propylene Oxide	MO
Allyl Chloride	MO	Cyclohexanol	MO	Isobutanol	O	Pyrolysis Gasoline	O
Ammonia	MO	Cyclohexanone	MO	Isobutylene	IMO	Sodium Chloride	O
Ammonium Bisulfate	O	Dichlorodifluoromethane	O	Isobutyraldehyde	MO	Sodium Hydroxide	I
Ammonium Chloride	O	Diethylene Glycol	O	Isopentanes	I	Sodium Sulfite	O
Ammonium Sulfate	O	Dimethyl Terephthalate	O	Isophthalic Acid	O	Styrene	O
Aniline	O	Dinitrotoluene	MO	Isoprene	O	Sulfur	IMO
Benzene	IMO	Epichlorohydrin	MO	Isopropanol	MO	Sulfuric Acid	I
Benzoic Acid	MO	Ethane	I	Ketene	MO	Terephthalic Acid	MO
Bisphenol-A	O	Ethanol	MO	Maleic Anhydride	MO	Toluene	IMO
Bromine	I	Ethyl Acetate	O	Methane	IMO	Toluene Diamine	MO
Butadiene	MO	Ethyl Acrylate	O	Methanol	MO	Toluene Diisocyanate	O
n-Butane	IMO	Ethylbenzene	MO	Methyl Chloride	MO	Trichloroethylene	MO
n-Butanol	O	Ethyl Chloride	O	Methyl Chloroform	O	Trichlorofluoromethane	O
s-Butanol	MO	Ethylene	MO	Methylene Dichloride	O	Triethylene Glycol	O
n-Butylenes	IMO	Ethylene Dibromide	O	Methyl Ethyl Ketone	O	Urea	O
n-Butyraldehyde	MO	Ethylene Dichloride	MO	Methyl Isobutyl Ketone	O	Vinyl Acetate	O
Calcium Chloride	O	Ethylene Glycol	O	Methyl Methacrylate	O	Vinyl Chloride	MO
Calcium Hydroxide	I	Ethylene Oxide	MO	Naphtha	I	m-Xylene	IMO
Calcium Hypochlorite	I	2-Ethylhexanol	O	Naphthalene	I	o-Xylene	IMO
Caprolactam	O	Formaldehyde	MO	Nitric Acid	I	p-Xylene	IMO

Table 2. A list of the chemical transformations constituting the model industry.

1. Acetaldehyde via oxidation of ethylene
2. Acetaldehyde via dehydrogenation of ethanol
3. Acetaldehyde via oxidation of ethanol
4. Acetaldehyde via oxidation of propane
5. Acetaldehyde via oxidation of n-butane
6. Acetaldehyde via hydration of acetylene
7. Acetic acid via oxidation of n-butane
8. Acetic acid via oxidation of acetaldehyde
9. Acetic acid via carbonylation of methanol
10. Acetic acid via oxidation of naphtha
11. Acetic acid via oxidation of n-butylenes
12. Acetic anhydride via reaction of ketene and acetic acid
13. Acetic anhydride via oxidation of acetaldehyde
14. Acetic anhydride via reaction of acetylene and acetic acid
15. Acetone via dehydrogenation of isopropanol
16. Acetone via oxidation of isopropanol
17. Acetone via oxidation of propylene
18. Acetone via hydration of acetylene
19. Acetone via hydration of ethanol
20. Acetone via decarboxylation of acetic acid
21. Acetylene via pyrolysis of methane
22. Acetylene via pyrolysis of ethane
23. Acetylene via pyrolysis of propane
24. Acetylene via pyrolysis of n-butane
25. Acetylene via pyrolysis of naphtha
26. Acrolein via oxidation of propylene
27. Acrolein via reaction of formaldehyde and acetaldehyde
28. Acrylic acid via oxidation of acrolein
29. Acrylic acid via carbonylation of acetylene
30. Acrylic acid via reaction of formaldehyde and ketene
31. Acrylic acid via sulfenation of acrylonitrile
32. Acrylic acid via cyanation of ethylene oxide
33. Acrylonitrile via ammoxidation of propylene
34. Acrylonitrile via cyanation of acetylene
35. Acrylonitrile via cyanation of ethylene oxide
36. Adipic acid via oxidation of cyclohexanone
37. Adipic acid via oxidation of cyclohexanol
38. Adiponitrile via reaction of adipic acid and ammonia
39. Adiponitrile via chlorination of butadiene
40. Adiponitrile via hydrodimerization of acrylonitrile
41. Allyl alcohol via reaction of acrolein and isopropanol
42. Allyl alcohol via isomerization of propylene oxide
43. Allyl alcohol via hydrolysis of allyl chloride
44. Allyl chloride via chlorination of propylene
45. Ammonia from reaction of hydrogen and nitrogen
46. Aniline via hydrogenation of nitrobenzene
47. Aniline via reaction of ammonia and chlorobenzene
48. Benzene via hydrodealkylation of toluene
49. Benzene via disproportionation of toluene
50. Benzoic acid via oxidation of toluene
51. Benzoic acid via decarboxylation of phthalic anhydride
52. Benzoic acid via chlorination of toluene
53. Bisphenol-A via reaction of phenol and acetone
54. Butadiene via dehydrogenation of n-butylenes
55. Butadiene via dehydrogenation of n-butane
56. Butadiene via reaction of ethanol and acetaldehyde
57. Butadiene via dimerization of acetaldehyde
58. Butadiene via reaction of acetylene and formaldehyde
59. n-Butanol via hydrogenation of n-butyraldehyde
60. s-Butanol via hydration of n-butylenes
61. n-Butyraldehyde via oxoation of propylene
62. n-Butyraldehyde via dimerization of acetaldehyde
63. Caprolactam via reaction of cyclohexanone and hydroxylamine
64. Caprolactam via reaction of cyclohexanone and peracetic acid
65. Caprolactam via nitrosation of cyclohexane
66. Caprolactam via hydrogenation and nitrosation of benzoic acid
67. Carbon disulfide via reaction of methane and sulfur
68. Synthesis gas via reforming of methane
69. Synthesis gas via reforming of naphtha
70. Carbon dioxide and hydrogen via water-gas shift reaction
71. Carbon tetrachloride via chlorination of methane
72. Carbon tetrachloride via chlorination of carbon disulfide
73. Carbon tetrachloride via chlorinolysis of propane
74. Carbon tetrachloride via chlorinolysis of propylene dichloride
75. Chlorobenzene via chlorination of benzene
76. Chlorobenzene via hydrochlorination of benzene
77. Chloroform via chlorination of methane
78. Chloroform via reaction of acetone and calcium hypochlorite
79. Chloroform via reaction of ethanol and calcium hypochlorite
80. Chloroform via chlorination of methyl chloride
81. Chloroprene via chlorination of butadiene
82. Chloroprene via dimerization of acetylene
83. Cumene via reaction of benzene and propylene
84. Cresylic acid via methylation of phenol
85. Cresylic acid via reaction of toluene and propylene
86. Cyclohexane via hydrogenation of benzene
87. Cyclohexanol via oxidation of cyclohexane
88. Cyclohexanol via hydrogenation of phenol
89. Cyclohexanol via hydrogenation of cyclohexanone
90. Cyclohexanone via dehydrogenation of cyclohexanol
91. Cyclohexanone via hydrogenation of phenol
92. Dichlorodifluoromethane via reaction of carbon tetrachloride and hydrogen fluoride
93. Dimethyl terephthalate via esterification of terephthalic acid with methanol
94. Dimethyl terephthalate via reaction of methanol and p-xylene

of toluene
n of toluene
toluene
ion of phthalic anhydride
of toluene
henol and acetone
of n-butylenes
of n-butane
nol and acetaldehyde
acetaldehyde
ylene and formaldehyde
n-butyraldehyde
utylenes
f propylene
on of acetaldehyde
clohexanone and hydroxylamine
clohexanone and peracetic acid
cyclohexane
and nitrosation of benzoic acid
of methane and sulfur
methane
naphtha
water-gas shift reaction
ination of methane
ination of carbon disulfide
nolysis of propane
nolysis of propylene dichloride
of benzene
tion of benzene
methane
one and calcium hypochlorite
nol and calcium hypochlorite
methyl chloride
butadiene
acetylene
and propylene
f phenol
oluene and propylene
f benzene
yclohexane
f phenol
f cyclohexanone
n of cyclohexanol
of phenol
tion of carbon tetrachloride

ification of terephthalic acid

ion of methanol and p-xylene

Table 2 Continued

95. Dinitrotoluene via nitration of toluene
96. Epichlorohydrin via chlorination of allyl chloride
97. Ethanol via hydration of ethylene
98. Ethanol via sulfonation of ethylene
99. Ethyl acetate via esterification of acetic acid with ethanol
100. Ethyl acetate via dimerization of acetaldehyde
101. Ethyl acrylate via esterification of acrylic acid with ethanol
102. Ethylbenzene via reaction of benzene and ethylene
103. Ethyl chloride via hydrochlorination of ethylene
104. Ethyl chloride via chlorination of ethane
105. Ethyl chloride via hydrochlorination of ethanol
106. Ethylene via pyrolysis of ethane
107. Ethylene via pyrolysis of propane
108. Ethylene via pyrolysis of n-butane
109. Ethylene via high-severity pyrolysis of naphtha
110. Ethylene via low-severity pyrolysis of naphtha
111. Ethylene via high-severity pyrolysis of gas oil
112. Ethylene via low-severity pyrolysis of gas oil
113. Ethylene via hydrogenation of acetylene
114. Ethylene via dehydration of ethanol
115. Ethylene dibromide via bromination of ethylene
116. Ethylene dichloride via chlorination of ethylene
117. Ethylene dichloride via hydrochlorination of ethylene
118. Ethylene glycol via hydration of ethylene oxide
119. Ethylene glycol via carbonylation of formaldehyde
120. Ethylene oxide via oxidation of ethylene
121. Ethylene oxide via chlorohydration of ethylene
122. 2-Ethylhexanol via dimerization of n-butyraldehyde
123. Formaldehyde via oxidation of methanol
124. Formaldehyde via dehydrogenation of methanol
125. Fumaric acid via isomerization of maleic anhydride
126. Glycerin via hydrolysis of epichlorohydrin
127. Glycerin via reaction of allyl alcohol and hydrogen peroxide
128. Hexamethylenediamine via hydrogenation of adiponitrile
129. Hydrogen cyanide via reaction of methane and ammonia
130. Isobutanol via hydrogenation of isobutyraldehyde
131. Isophthalic acid via oxidation of m-xylene
132. Isoprene via dehydrogenation of isopentenes
133. Isoprene via dimerization of propylene
134. Isoprene via reaction of formaldehyde and isobutylene
135. Isopropanol via sulfonation of propylene
136. Isopropanol via hydration of propylene
137. Ketene via pyrolysis of acetic acid
138. Ketene via pyrolysis of acetone
139. Maleic anhydride via oxidation of benzene
140. Maleic anhydride via oxidation of n-butylenes
141. Methanol via hydrogenation of carbon monoxide
142. Methanol via hydrogenation of carbon dioxide
143. Methyl chloride via chlorination of methane
144. Methyl chloride via hydrochlorination of methanol
145. Methyl chloroform via chlorination of ethylene dichloride
146. Methyl chloroform via chlorination of vinyl chloride
147. Methylene dichloride via chlorination of methane
148. Methylene dichloride via chlorination of methyl chloride
149. Methyl ethyl ketone via dehydrogenation of s-butanol
150. Methyl ethyl ketone via oxidation of n-butylenes
151. Methyl isobutyl ketone via dimerization of acetone
152. Methyl methacrylate via cyanohydration of acetone
153. Methyl methacrylate via reaction of methanol and isobutylene
154. Nitrobenzene via nitration of benzene
155. Peracetic acid via oxidation of acetaldehyde
156. Peracetic acid via reaction of acetic acid and hydrogen peroxide
157. Perchloroethylene via chlorination of trichloroethylene
158. Perchloroethylene via chlorinolysis of propane
159. Perchloroethylene via chlorinolysis of propylene dichloride
160. Phenol via oxidation of cumene
161. Phenol via decarboxylation of benzoic acid
162. Phenol via dehydrochlorination of chlorobenzene
163. Phenol via alkaline hydrolysis of chlorobenzene
164. Phenol via sulfonation of benzene
165. Phosgene via reaction of chlorine and carbon monoxide
166. Phthalic anhydride via oxidation of o-xylene
167. Phthalic anhydride via oxidation of naphthalene
168. Propylene dichloride via chlorination of propylene
169. Propylene glycol via hydration of propylene oxide
170. Propylene oxide via chlorohydration of propylene
171. Propylene oxide via reaction of propylene and isobutane
172. Styrene via dehydrogenation of ethyl-benzene
173. Terephthalic acid via oxidation of p-xylene
174. Terephthalic acid via disproportionation of benzoic acid
175. Toluene diamine via hydrogenation of dinitrotoluene
176. Toluene diisocyanate via phosgenation of toluene diamine
177. Trichloroethylene via chlorination of ethylene dichloride
178. Trichloroethylene via chlorination of acetylene
179. Trichlorofluoromethane via reaction of carbon tetrachloride and hydrogen fluoride.
180. Urea via reaction of ammonia and carbon monoxide
181. Vinyl acetate via reaction of acetylene and acetic acid
182. Vinyl acetate via reaction of ethylene and acetic acid
183. Vinyl acetate via reaction of acetaldehyde and acetic anhydride
184. Vinyl chloride via dehydrochlorination of ethylene dichloride
185. Vinyl chloride via hydrochlorination of acetylene
186. Vinyl chloride via chlorination of ethane

Table 3. The feedstock efficiency indices for three cases: (a) the bounding industry which minimizes the consumption of feedstock carbon, (b) the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and naphtha and gas oil are made available as a replacement, (c) the perturbation of the bounding industry in which natural gas is eliminated as a feedstock and coal-derived methane and synthesis gas are made available as a replacement.

Chemical	case (a)	case (b)	case (c)
Acetaldehyde	.82	.70	.37
Acetic Acid	1.48	1.29	5.00
Acetone	1.05	.93	3.44
Acetylene	.60	.47	.36
Acrylic Acid	1.06	.93	12.5
Acrylonitrile	.65	.63	.70
Adiponitrile	.58	.57	.64
Aniline	.82	.82	.95
Butadiene	.66	.89	.51
n-Butyraldehyde	.83	.71	.82
Caprolactam	.62	.58	.91
Carbon Tetrachloride	1.00	.80	1.00
Chloroprene	.50	.68	.39
Ethanol	.81	.68	.28
Ethylene	.88	.74	.31
Ethylene Oxide	.72	.61	.25
Isoprene	.87	∞	2.51
Maleic Anhydride	.43	.45	.45
Methyl Ethyl Ketone	.66	.87	.54
Methyl Methacrylate	.73	3.75	1.71
Phenol	.80	.84	.84
Phthalic Anhydride	.71	.71	.71
Propylene Oxide	.75	.75	.76
Vinyl Acetate	1.06	.89	.66
Vinyl Chloride	.76	.63	.34