SECTION IV

INDUSTRY SUBCATEGORIZATION

Discussion of the Rationale of Subcategorization

The goal of this study is the development of effluent limitations commensurate with different levels of pollution control technology. These effluent limitations will specify the quantity of pollutants which will ultimately be discharged from a specific manufacturing facility and will be related to the quantity of raw materials consumed and the production methodology.

The diverse range of products and manufacturing processes to be covered suggests that separate effluent limitations be designated for different segments within the industry. To this end, a subcategorization of the Petroleum Refining Industry has been developed. The subcategorization is process oriented, with a delineation between subcategories based upon raw waste load characteristics in relation to the complexity of refinery operations.

Today's petroleum refinery is a very complex combination of interdependent operations and systems. In the development of a pollution profile for this industry, ten major process categories were listed as fundamental to the production of principal oil products (see listing in Table 8).

The American Petroleum Institute (API) has developed a classification system which utilizes this technology breakdown. They have tentatively divided U.S. refineries into 5 classifications, which primarily recognize varying degrees of processing complexity and resultant distribution of products. The present API classification system is as follows:

Class	Process Complexity
A	Crude Topping
B	Topping and Cracking
C	Topping, cracking, and petrochemicals
D	"B" Category, and lube oils processing
E	"D" Category, and petrochemicals

Development of Industry Subcategorization

Age, size, and waste water treatability of refineries were considered during the subcategorization of the refining industry. However, subcategorization by age is not necessarily useful, as additions to and modifications of refineries are the industry's principal form of expansion. Since most of the technology employed within the industry is of an evoluationary nature, refinery age was not a major factor in refinery subcategorization.

While the size of a refinery is important in terms of economical waste water treatment, the control technology employed in smaller refineries need not be as sophisticated a technology to achieve parity with larger refineries within the same subcategory.

Treatability characteristics of refinery waste waters indicate that these waste waters are generally amenable to excellent degrees of removal of pollutants. Since this is an industry-wide characteristic, the proper place to evaluate the subcategorization of the industry is with the raw waste load delivered to the refinery waste water treatment plant. The 1972 National Petroleum Refining Waste Water Characterization Studies of 135 refinery API separator effluents, provides a major tool for this evaluation. Attempts to explain and justify the differences based solely on type and method of cooling, inplant pretreatment, and housekeeping practices were also fruitless. However, generally speaking those refineries with good practices in all these areas did have the lower waste loadings.

In an attempt to determine the effects of process technology, a further analysis was made of the API individual or combined categories to evaluate the raw waste load as a function of the degree of cracking employed within the refinery. The operations included in degree of cracking were: thermal operations, catalytic cracking and hydroprocessing. The degree of cracking was expressed as percentage capacity of the total feedstock processing capacity within the refinery. The data for evaluating the net raw waste loads by this criteria were obtained by analyzing the raw waste load surveys supplied by refineries, literature sources, and analysis of the 1972 National Petroleum Refining Waste Water Characterization Studies.

Even though this new breakdown was a step in the right direction it did not explain raw waste load differences caused by the amount of cracking in the other subcategories and did not explain the effect of other process on the raw waste load. Therefore, the effort to further determine the effect of each refining process on the raw waste load continued.

Since the guideline is based on attainable flow rates and achievable concentrations based on each treatment technology, the effort was directed toward determining the relative flows expected from the many refining processes.

The approach taken, was the use of a multiple regression analysis using process and flow data from the 1972 National Petroleum Refining Waste Water Characterization Studies. The data consisted of waste water flows and individual process capacities for 94 refineries with less than 3 percent heat removal by once-through cooling. Those refineries with greater than 3 percent once-through cooling water were not used in order to eliminate as much of the non-process flow variation as possible.

The initial regressions carried out were in the form:

$$(1)\quad \frac{\text{Total Flow}}{\text{Capacity}} = A + B \sum Ci\ Pi$$

where A, B, and C are the constants to be determined from the regressions; Pi is the capacity of individual process categories relative to the refinery throughput and for each Pi there is a Ci which is the relative "weight" or importance of each process category in explaining the flow. The initial process breakdown used was supplied through the American Petroleum Institute and broke 126 individual process types into nine process categories.

Since the results of this initial form were not considered satisfactory, attempts were made to find out what other factors, if any, had explanatory power in predicting refinery flow. After many attempts, it was found that in addition to the process configuration of the refinery, the refinery size was an important factor in explaining the flow.

The final form of the equation which gave the best fit to the data was as follows:

$$(2)\quad \log \frac{\text{Total Flow}}{\text{Capacity (T)}} = A + BT + C \sum Di\ Pi$$

where T or capacity is equal to the refinery throughput; A, C, Di and Pi are the same as A, B, Ci and Pi, respectively, in the initial regression form; and B is a constant.

Adjustments were then made to the API breakdown of the process categories to improve the fit to the data. The 126 individual processes were finally put into one of the following nine process categories:

1. crude processes
2. cracking processes
3. hydrocarbon processing
4. lubes and greases
5. coking processes
6. treating and finishing processes
7. first generation petrochemicals
8. second generation petrochemicals
9. asphalt production

It was found that only crude processes, cracking processes, lubes and greases, coking processes, second generation petrochemicals and asphalt production showed significance in the regression. In addition, even though second generation petrochemicals showed significance, the Di or "weighting factor" for it was -6. The nonsignificant processes and second generation petrochemicals were therefore given 0 (zero) weighting factors.

The Di's or weighting factors for the significant process categories are as follows: crude process +1; cracking and coking processes +6; lubes and greases +13; and asphalt production +12.

A breakdown of the individual process in each process category is contained in Table 51.

The values for constants B and C were then obtained by regressing against flow with equation (2) with the Di value defined as above. The resulting values are B=1.51 and C=0.0738. The magnitude of A has no significance since the analysis is to be used only within each subcategory and not across all subcategories. (Fitting the actual flows with those predicted was tried both using the analysis across the entire industry and within each subcategory, with the results being much better using it only to explain differences within subcategories).

The above results were then put into a usable form by taking the anti log of equation (2), which is

$$(3)\quad \text{flow(gal/bbl)} = A10^{BT}\,10^{C\,\mathcal{E}\,DiPi}$$

The constant A is now the 50 percent probability flow (gal/bbl) which was used previously to calculate the limits for each subcategory. To apply this to each subcategory (to determine the variance needed for each case from the average refinery in each subcategory) the average size (Ta) and process configuration ([$\mathcal{E}$ DiPi]a) for each subcategory was calculated. The range of sizes and process configurations were then divided up into ranges and the midpoint of each range was then compared to the average for that subcategory to calculate the size and process factor for that range (see below).

$$10^{BT} = 10^{1.51(Ti-Ta)}$$

$$10^{C\,\mathcal{E}\,DiPi} = 10^{0.0738[(\mathcal{E}\,DiPi)j-(\mathcal{E}\,DiPi)a]}$$

where Ti is the midpoint of that particular size range; Ta is the average size in the subcategory, with both Ta and Ti in millions of barrells per day; [$\mathcal{E}$ DiPi]i is the midpoint of that particular process configuration range; and [$\mathcal{E}$ DiPi]a is the average process configuration of the subcategory.

Further analysis of the data showed a break in the significance of size in explaining flow for those refineries over 150,000 bbl/day. This means that over 150,000 bbl/day only the process configuration has significance in explaining the flows. As a result the size ranges where broken off at either 150,000 bbl/day or the average refinery size in a subcategory, whichever was greater.

An example of the application of the size and process factors is in section IX. The basic data used, regressions run, etc. are in Supplement B "Refinery Configuration Analysis".

The size and process factors are in Table 1 - 5, Section II.

Subcategorization Results

Using the procedures outlined above, many trials were performed in order to obtain a subcategorization of the petroleum refining industry which is reflective of the net raw waste load with respect to type of refinery (function), process technology employed, and severity of operations. The final subcategorization obtained from this analysis is indicated below in Table 16. Detailed probability plots for the development of the subcategorization are contained in supplement B.

For each of these new subcategories the parameters for the selected median values are indicated in Table 17. A further enumeration of overall net raw waste load characteristics is given in Section V.

Analysis of the Subcategorization

Topping subcategory

The topping subcategory is similar to the previous API category A in that it does not include any refineries with cracking or coking processes. That is to say it includes all refineries which combine all other porcesses except cracking and coking.

Cracking subcategory

API Category B includes refineries which contain topping, reforming, and cracking operations. Also included are all first generation conventional refinery-associated products or intermediates, such as benzene-toluene-xylene (BTX), alkanes, alkenes, alkynes, and other miscellaneous items such as sulfur, hydrogen and coke.

Subcategory B as defined here is the same as API category B execpt that the inclusion of first generation petrochemicals shall only be for those whose production amounts to less than 15 percent of the refinery throughput.

Petrochemical subcategory

The petrochemical subcategory is similar to the API category C. Operations included within this subcategory are topping,

TABLE 16

Subcategorization of the Petroleum Refining Industry Reflecting Significant Differences in Waste Water Characteristics

Subcategory	Basic Refinery Operations Included
Topping	Topping and catalytic reforming whether or not the facility includes any other process in addition to topping and catalytic process. This subcategory is not applicable to facilities which include thermal processes (coking, visbreaking, etc.) or catalytic cracking.
Cracking	Topping and cracking, whether or not the facility includes any processes in addition to topping and cracking, unless spefified in one of the subcategories listed below.
Petrochemical	Topping, cracking and petrochemical operations, whether or not the facility includes any process in addition to topping, cracking and petrochemical operations,* except lube oil manufacturing operations.
Lube	Topping, cracking and lube oil manufacturing processes, whether or not the facility includes any process in addition to topping, cracking and lube oil manufacturing processes, except petrochemical operations.*
Integrated	Topping, cracking, lube oil manufacturing processes, and petrochemical operations, whether or not the facility includes any processes in addition to topping, cracking, lube oil manufacturing processes and petrochemical operations.*

* The term "petrochemical operations" shall mean the production of second generation petrochemicals (i.e., alcohols, ketones, cumene, styrene, etc.) or first generation petrochemicals and isomerization products (i.e., BTX, olefins, cyclohexane, etc.) when 15% or more of refinery production is as first generation petrochemicals and isomerization products.

TABLE 17

NET RAW WASTE LOADS FROM PETROLEUM REFINING INDUSTRY CATEGORIES (50 Percent Probability of Occurrence)

KILOGRAMS/10000 M^3 (LB/1000 BBLS)

SUBCATEGORY	BOD5	OIL/GREASE	PHENOL	AMMONIA
TOPPING	3.43(1.2)	8.29(2.9)	0.034(0.012)	1.20(0.42)
CRACKING	72.93(25.5)	31.17(10.9)	4.00(1.4)	28.31(9.9)
PETROCHEMICAL	171.6(60)	52.91(18.5)	7.72(2.7)	34.32(12)
LUBE	217(76)	120.1(42)	8.3(2.9)	24.1(8.5)
INTEGRATED	197(69)	75(26)	3.8(1.3)	20.5(7.2)

cracking, and petrochemical operations. Petrochemical operations include first generation conventional refinery-associated production, as described in the cracking subcategory, but only when it amounts to greater than 15 percent of the refinery throughput. This takes into consideration the additional cooling tower blowdown from this operation. Intermediate chemical production, including such typical products as cumene, phthalic anhydride, alcohols, ketones, trimer, and styrene, shall be considered second generation petrochemical operations and classify a refinery in this subcategory.

Lube subcategory

The lube subcategory is the same as the API category D.

In the lube subcategory, the operations included under the cracking subcategory are expanded to include lube oil manufacturing processes. Lube oil processing excludes formulating blended oils and additives.

Integrated subcategory

The integrated subcategory is the same as API category E, except for the definition of petrochemical operatons specified in the petrochemical subcategory.

Conclusion

The subcategorization of the petroleum refinery industry presented above allows for the definition of logical segments of the industry in terms of factors which effect generated API separator effluent waste water quality. It allows for rapid identification of the expected median net raw waste loads as a basis for developing effluent guidelines for the discharge from the individual refinery. The subcategorization determined above is used throughout this report as the basis for development of effluent limitations and guidelines.