

EPA-450/3-77-046

August 1976

**SCREENING STUDY
TO DETERMINE NEED
FOR SO_x AND HYDROCARBON
NSPS FOR FCC
REGENERATORS**



**U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711**

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NSPS FOR FCC REGENERATORS**

by

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**Contract No. 68-02-1332
Task No. 22**

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Prepared for

**U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711**

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Publication No. EPA-450/3-77-046

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EXECUTIVE SUMMARY

PURPOSE AND SCOPE

Section 111 of the Clean Air Act charges the Administrator of the Environmental Protection Agency (EPA) with the responsibility of establishing Federal standards of performance for new stationary sources which may significantly contribute to air pollution. These new source performance standards (NSPS) are to reflect the degree of emission limitation achievable through application of the best demonstrated control methods considering cost.

The Scope of this task order is twofold: (1) to identify and present all available data that would define the emission levels that can be achieved with the most effective demonstrated control systems, and (2) to estimate the emission reductions that would result through promulgation of new source performance standards for Fluid Catalytic Cracking (FCC) units used by the petroleum refining industry. The results of this task will be used as part of the EPA's assessment of numerous industries for the purpose of establishing priorities for setting standards.

OVERVIEW OF FLUID CATALYTIC CRACKING (FCC)

As of late 1975, the U.S. petroleum refining industry had an aggregate FCC charge capacity of 5.67 million barrels per stream day (BPSD) fresh feed and recycle, of which recycle accounted for 16%. Some sort of hydro-treating is currently performed on 6% of the fresh feed. Our investigation indicated that there is no accurate audit of the number of CO boilers installed on FCC units. A rough estimate is that 60-70% of the capacity has them.

Improved catalyst regeneration by High Temperature Regeneration (HTR) is the latest technology advancement being applied to FCC units. Based on interviews with industry representatives, it is estimated that HTR is being applied to about 15% of the domestic FCC capacity. This is expected to increase over the 10 year period considered in this evaluation.

In general, FCC capacity in the United States is not expected to show significant growth over this period. Growth rates of 0.5-1.5% per year are projected through 1985.

POLLUTANTS CONSIDERED

The pollutants assessed under this task include carbon monoxide, particulates, NO_x, SO_x, and hydrocarbons, with emphasis on the last two. NSPS currently exist for CO emissions from FCC units. The level of control was established to be consistent with that attainable with HTR, thereby including this technology as a method of control. The current control level for CO has a logical basis and no modification seems warranted.

The net reduction in 1985 of NSPS for SO_x is 49 to 85,000 tons/year depending on whether the level of control is set at 300 or 500 ppm. The impact is small due to the relatively small growth rate of new capacity and the low rate of replacement of existing facilities. No net reduction is expected from the application of NSPS for hydrocarbons since all new or substantially modified FCC units installed after 1975 will likely utilize either HTR or CO boiler technology. Hence, the emissions with NSPS based on best technology will be the same as the effective emissions without NSPS.

APPLICABILITY OF NSPS TO MODIFIED SOURCES

One of the issues addressed in this assessment was whether a FCC modification such as revamping for HTR would constitute a major reconstruction as defined in the Federal Register. One of our industry contacts noted that the wording of the regulation can be interpreted in such a way as to imply that the affected facility is only the regenerator not the entire FCC unit.* The key point is whether the cost of revamping a FCC regenerator is more than 50% of the cost of a new regenerator or FCC unit depending on how one interprets the law.

The results of cursory review of typical costs for FCC regenerator modifications and new equipment are presented in Table 2. The cost of revamping the regenerator is approximately 15% of the cost of a new facility (regenerator only). Even if the revamp costs 2 to 3 times the figure shown, it would not be classified as a major reconstruction, even with a narrow interpretation of the regulations. Consequently, NSPS will not generally apply to reconstructed FCC units based on current practice.

*Informal discussions with the EPA indicates that their interpretation encompasses the entire FCC unit, since the catalyst regenerator is an integral part of the system.

TABLE 2

ESTIMATED COST OF FCC REGENERATOR
MODIFICATIONS AND NEW EQUIPMENT

Capacity - 45,000 Bbl/Day

	<u>New</u>	<u>Modified</u>
Capital Investment ¹ (1975)		\$10 ⁶
New FCC Unit	21.6	--
Regenerator	8.6	1.2
Modified - Percent of New	--	14

¹Materials and labor.

Source: Hydrocarbon Processing, 1974 Refining Handbook, and Exxon R&E.

I. THE PETROLEUM REFINING INDUSTRY

The stated purpose of this study is to estimate the atmospheric emission reduction of potential New Source Performance Standards (NSPS) for SO_x and hydrocarbon emissions from fluid catalytic cracker (FCC) regenerators. In order to do this it is necessary to first identify the FCC population and some of the factors which bear on the emissions. In this chapter we present this information.

A. EXISTING FLUID CATALYTIC CRACKING UNITS

As of December 1975, the U.S. petroleum refining industry consisted of 256 refineries with a total crude capacity of 15,687,000 barrels per stream day (BPSD).⁹ One hundred and forty-three of these facilities have fluid catalytic cracking units (FCCU), which are the focus of this study. The aggregate FCC charge capacity is 5,675,100 BPSD⁹ fresh feed plus recycle. Table I-1 shows the location of refineries with FCC units (by state and city), the operating company, total FCC capacity of the refinery (some refineries have multiple FCC units), and the type of catalytic cracking technology used.

Table I-2 shows the geographical distribution of FCC capacity by state and Petroleum Administration for Defense (PAD) District and the percentage of total U.S. capacity by PAD. (See Figure I-1 for PAD Districts.) PAD's II and III together contain almost three-quarters of the total capacity, with PAD IV containing only 4%. Another useful way of breaking down the FCC population is by Air Quality Control Region (AQCR). A map of these AQCR regions and a table showing the relationship between AQCR and PAD districts may be found at the beginning of Appendix C.

With regard to individual FCC capacity, the average (total capacity/number of units) is approximately 50,000 BPSD. However, seventy-five percent of all FCC units are smaller than the average capacity so a typical facility would be less than 50,000 BPSD.

B. GENERAL OPERATING FACTORS

Total capacity consists of both fresh feed and recycle. According to The Oil and Gas Journal figures, 930,190 BPSD, or 16% of the total, is recycle. FCC recycle ratios are strongly dependent on the type of catalyst used, but have generally been declining as a result of the improved activity afforded by zeolite catalysts. Recycle rates in the range of 5-15% of fresh feed are common for operations utilizing zeolitic catalyst. A 5% recycle is about the practical minimum since some cycle oil is required to return the catalyst that is entrained into the fractionator with the reactor effluent.

Six percent of total FCC fresh feed is hydrotreated. The distribution of feed hydrotreating by PAD district is shown in Table I-3.

TABLE I-1

LOCATION OF U.S. FLUID CATALYTIC CRACKING CAPACITY

(as of 12/31/75)

<u>Location</u>	<u>Operating Company</u>	<u>Process Type</u>	<u>Fresh Feed (BPSD)</u>	<u>Fresh Feed + Recycle (BPSD)</u>
<u>Arkansas</u>				
El Dorado	Lions Oil Co.	Fluid	15,000	18,000
<u>California</u>				
Carson	Atlantic Richfield Co.	Fluid	57,000	65,000
Benicia	Exxon Co.	Fluid	45,000	58,000
Santa Fe Springs	Gulf Oil Co.	Fluid	13,500	13,800
Torrance	Mobil Oil Corp.	Fluid	56,000	56,000 ²
Martinez	Phillips Petroleum Co.	Fluid	47,000	47,000 ^{1,2}
Santa Fe Springs	Powerine Oil Co.	Fluid	11,000	12,000
Martinez	Shell Oil Co.	Fluid	46,000	86,000
Wilmington	Shell Oil Co.	Fluid	35,000	40,000
El Segundo	Standard Oil Co. of California	Fluid	43,500	54,500 ¹
Richmond	Standard Oil Co. of California	Fluid	43,500	54,500 ¹
Wilmington	Texaco, Inc.	Fluid	28,000 ¹	28,000 ^{1,2}
Bakersfield	Tosco Petro Corp.	Thermoform	12,000	12,000 ³
Los Angeles	Union Oil Co. of California	Fluid	45,000	52,000
<u>Colorado</u>				
Denver	Continental Oil Co.	Fluid	15,000	16,000
Commerce City	The Refinery Corp.	Fluid	75,000	7,900
<u>Delaware</u>				
Delaware City	Getty Oil Co., Inc.	Fluid	62,000	77,000
<u>Hawaii</u>				
Barbers Point	Standard Oil Co. of California	Fluid	14,100	23,000
<u>Illinois</u>				
Wood River	Amoco Oil Co.	Fluid	38,000	42,000
Blue Island	Clark Oil & Refining Corp.	Fluid	24,000	25,000

¹BPCD; BPSD not recorded.²Recycle not recorded.³No recycle.

TABLE I-1 cont'd
LOCATION OF U.S. FLUID CATALYTIC CRACKING CAPACITY
(as of 12/31/75)

<u>Location</u>	<u>Operating Company</u>	<u>Process Type</u>	<u>Fresh Feed</u> (BPSD)	<u>Fresh Feed + Recycle</u> (BPSD)
<u>Illinois cont'd</u>				
Hartford	Clark Oil & Refining Corp.	Fluid	26,000	27,000
Robinson	Marathon Oil Co.	Fluid	36,500	44,500
Joliet	Mobil Oil Co.	Fluid	85,000	85,000 ²
Wood River	Shell Oil Co.	Fluid	94,000	94,000 ²
Lawrenceville	Texaco, Inc.	Fluid	31,000 ¹	31,000 ^{1,2}
Lockport	Texaco, Inc.	Fluid	30,000 ¹	30,000 ^{1,2}
Lemont	Union Oil Co. of California	Fluid	58,000	66,000
<u>Indiana</u>				
Whiting	Amoco Oil Co.	Fluid	123,000	130,000
E. Chicago	Atlantic Richfield Co.	Fluid	48,000	50,000
Mount Vernon	Indiana Farm Bureau Cooperative Association, Inc.	Fluid	6,000	6,000 ²
Indianapolis	Rock Island Refining Corp.	Fluid	16,000	16,000 ²
<u>Kansas</u>				
El Dorado	American Petrofina, Inc.	Fluid	11,000	11,500
Arkansas City	Apco Oil Corp.	Fluid	9,400	10,200
Coffeyville	CRA Inc.	Fluid	14,500	16,000
Phillipsburg	CRA Inc.	Fluid	8,000	8,600
Wichita	Derby Refining Co.	Fluid	10,800	12,500
Augusta	Mobil Oil Corp.	Thermofoor	21,500	23,500
McPherson	National Cooperative Refinery Association	Fluid	20,000	21,000
Shallow Water	North American Petroleum Corp.	Thermofoor	5,500	5,500 ²
Kansas City	Phillips Petroleum Corp.	Fluid	32,000	48,000
El Dorado	Skelly Oil Co.	Fluid	31,000	48,000
<u>Kentucky</u>				
Catlettsburg	Ashland Petroleum Co.	Fluid	54,000	55,000
<u>Louisiana</u>				
Lake Charles	Cities Service Oil Co.	Fluid	125,000	145,000
Lake Charles	Continental Oil	Thermofoor	27,000	32,000

TABLE I-1 cont'd

LOCATION OF U.S. FLUID CATALYTIC CRACKING CAPACITY
(as of 12/31/75)

<u>Location</u>	<u>Operating Company</u>	<u>Process Type</u>	<u>Fresh Feed (BPSD)</u>	<u>Fresh Feed + Recycle (BPSD)</u>
<u>Louisiana cont'd</u>				
Baton Rouge	Exxon Co.	Fluid	169,000	169,000 ³
Metairie	Good Hope Refineries, Inc.	Fluid	8,500	8,500 ²
Belle Chasse Alliance Refinery	Gulf Oil Co.	Fluid	78,000	80,300
Meraux	Murphy Oil Corp.	Fluid	10,500	11,000
Norco	Shell Oil Co.	Fluid	100,000	102,000
Chalmette	Tenneco Oil Co.	Fluid	22,000	22,000 ²
Convent	Texaco Inc.	Fluid	70,000 ¹	70,000 ^{1, 2}
<u>Michigan</u>				
Bay City	Bay Refining-Dow Chemical, USA	Thermoform	6,000	8,000
Detroit	Marathon Oil Co.	Fluid	21,500	25,400
Alma	Total Leonard Inc.	Fluid	12,000	13,500
<u>Minnesota</u>				
Wrenshall	Continental Oil Co.	Fluid	9,500	10,000
Pine Bend	Koch Refining Co.	Fluid	41,000	42,000
St. Paul Park	Northwestern Refining Co., Division of Ashland	Fluid	21,000	22,500
<u>Mississippi</u>				
Purvis	Ameralda-Hess Corp.	Thermoform	14,500	14,500 ²
Pascagoula	Standard Oil Co. of Kentucky	Fluid	56,000	58,000
<u>Missouri</u>				
Sugar Creek	Amoco Oil Co.	Fluid	41,000	53,000
<u>Montana</u>				
Laurel	Ceney	Fluid	11,500	14,500
Billings	Continental Oil Co.	Fluid	14,000	21,000
Billings	Exxon Co.	Fluid	19,000	34,000
Great Falls	Phillips Petroleum Co.	Fluid	1,800	3,000

TABLE I-1 cont'd

LOCATION OF U.S. FLUID CATALYTIC CRACKING CAPACITY

(as of 12/31/75)

<u>Location</u>	<u>Operating Company</u>	<u>Process Type</u>	<u>Fresh Feed</u> (BPSD)	<u>Fresh Feed + Recycle</u> (BPSD)
<u>Nebraska</u>				
Scottsbluff	CRA, Inc.	Fluid	2,400	2,900
<u>New Jersey</u>				
Perth Amboy	Chevron Oil Co.	Houdrifiow	30,000	38,000
Linden	Exxon Co.	Fluid	130,000	150,000
Paulsboro	Mobil Oil Corp.	Thermofofor	25,000	25,000 ³
Westville	Texaco Inc.	Fluid	40,000 ¹	40,000 ²
<u>New Mexico</u>				
Artesia	Navajo Refining Co.	Thermofofor	5,200	5,200 ²
Ciniza	Shell Oil Co.	Fluid	7,200	10,800
<u>New York</u>				
Tonawanda	Ashland Petroleum Co.	Fluid	22,000	22,000 ²
Buffalo	Mobil Oil Corp.	Thermofofor	19,000	25,000
<u>North Dakota</u>				
Mandan	Amoco Oil Co.	Fluid	23,000	34,000
<u>Ohio</u>				
Canton	Ashland Petroleum Co.	Fluid	24,460	25,200
Cleves	Gulf Oil Co.	Fluid	18,000	27,000
Toledo	Gulf Oil Co.	Fluid	19,800	21,800
Lima	Standard Oil Co. of Ohio	Fluid	37,700	45,500
Toledo	Standard Oil Co. of Ohio	Fluid	52,500	71,500
Toledo	Sun Oil Co. of Pennsylvania	Fluid	50,000	57,500
<u>Oklahoma</u>				
Cyril	Apco Oil Corp.	Fluid	6,700	8,375
Enid	Champlin Petroleum Co.	Fluid	19,000	19,300
Ponca City	Continental Oil Co.	Fluid	44,000	44,000 ²
Wynnewood	Kerr-McGee Corp.	Fluid	11,500	13,500
Cushing	Midland Cooperatives Inc.	Fluid	7,000	10,000
Okmulgee	OKC Refining Inc.	Thermofofor	8,000	10,000

TABLE I-1 cont'd

LOCATION OF U.S. FLUID CATALYTIC CRACKING CAPACITY

(as of 12/31/75)

<u>Location</u>	<u>Operating Company</u>	<u>Process Type</u>	<u>Fresh Feed (BPSD)</u>	<u>Fresh Feed + Recycle (BPSD)</u>
<u>Oklahoma cont'd</u>				
Duncan	Sun Oil Co.	Fluid	25,000	35,500
Tulsa	Sun Oil Co.	Fluid	30,000	31,400
West Tulsa	Texaco Inc.	Fluid	18,000 ¹	18,000 ^{1, 2}
Ardmore	Vickers Petroleum Corp.	Fluid	20,000	21,000
<u>Pennsylvania</u>				
Marcus Hook	BP Oil Corp.	Fluid	40,000	41,600
Philadelphia	Gulf Oil Corp.	Fluid	80,000	86,500
Marcus Hook	Sun Oil Co.	Fluid	75,000	85,000
Warren	United Refining Co.	Fluid	10,000	10,200
<u>Tennessee</u>				
Memphis	Delta Refining Co.	Thermoform	13,500	13,500 ³
<u>Texas</u>				
Mount Pleasant	American Petroleum Inc.	Thermoform	9,600	11,800
Port Arthur	American Petrofina, Inc.	Fluid	30,000	32,000
Texas City	Amoco Oil Co.	Fluid	157,000	204,000
Houston	Atlantic Richfield Co.	Fluid	69,000	74,000
Corpus Christi	Champlin Petroleum Co.	Fluid	13,000	13,105
Houston	Charter International Oil Co.	Fluid	24,000	29,000
El Paso	Chevron Oil Co.	Fluid	22,000	30,000
Corpus Christi	Coastal States Petrochemical Co.	Fluid	19,000	19,600
Big Spring	Cosden Oil & Chemical Co.	Fluid	24,000	25,000
Houston	Crown Central Petroleum Corp.	Fluid	43,000	52,000
Sunray	Diamond Shamrock Oil & Gas Co.	Thermoform	11,500	13,500
		Houdrifiow	11,500	13,500
Baytown	Exxon Co.	Fluid	125,000	146,000
Port Arthur	Gulf Oil Co.	Fluid	120,000	126,000
Tyler	La Gloria Gilt Gas Co.	Fluid	10,000	15,000
Texas City	Marathon Oil Co.	Fluid	28,500	33,000
Beaumont	Mobil Oil Co.	Fluid	84,000	84,000 ²
		Thermoform	24,000	24,000 ²
Borger	Phillips Petroleum Co.	Fluid	55,000	70,000
Sweeny	Phillips Petroleum Co.	Fluid	30,000	35,000

TABLE I-1 cont'd

LOCATION OF U.S. FLUID CATALYTIC CRACKING CAPACITY

(as of 12/31/75)

<u>Location</u>	<u>Operating Company</u>	<u>Process Type</u>	<u>Fresh Feed</u> (BPSD)	<u>Fresh Feed + Recycle</u> (BPSD)
<u>Texas cont'd</u>				
Deer Park	Shell Oil Co.	Fluid	70,000	70,000 ²
Odessa	Shell Oil Co.	Fluid	10,500	15,500
Corpus Christi	Southwestern Refining Co., Inc.	Fluid	9,500	12,000
Corpus Christi	Suntide Refining Co.	Fluid	20,000	26,500
Amarillo	Texaco, Inc.	Fluid	8,000 ¹	8,000 ^{1, 2}
El Paso	Texaco, Inc.	Fluid	7,000 ¹	7,000 ^{1, 2}
Port Arthur	Texaco, Inc.	Fluid	135,000 ¹	135,000 ^{1, 2}
Texas City	Texas City Refining Inc.	Fluid	27,000	28,000
Nederland	Union Oil Co. of California	Fluid	40,000	44,000
Fort Worth	Winston Refining Co.	Fluid	3,400	6,000
<u>Utah</u>				
Salt Lake City	Amoco Oil Co.	Fluid	18,000	22,000
Salt Lake City	Chevron Oil Co.	Fluid	10,000	11,000
		Houdrifiow	8,000	13,000
North Salt Lake	Husky Oil Co.	Thermofofor	4,400	6,900
Roosevelt	Plateau, Inc.	Fluid	5,200	5,200 ²
Woods Cross	Phillips Petroleum Co.	Thermofofor	8,000	10,500
<u>Virginia</u>				
Yorktown	Amoco Oil Co.	Fluid	27,000	32,000
<u>Washington</u>				
Ferndale	Mobil Oil Corp.	Thermofofor	25,500	27,500
Anacortes	Shell Oil Co.	Fluid	36,000	53,000
Anacortes	Texaco, Inc.	Fluid	27,000 ¹	27,000 ^{1, 2}
<u>Wisconsin</u>				
Superior	Murphy Oil Corp.	Fluid	9,700	10,700
<u>Wyoming</u>				
Casper	Amoco Oil Co.	Fluid	9,500	11,000
Cheyenne	Husky Oil Co.	Fluid	10,000	12,500
Cody	Husky Oil Co.	Fluid	3,300	4,300
Casper	Little America Refining Co.	Thermofofor	6,500	10,500
Sinclair	Pasco Inc.	Fluid	17,700	19,900
Newcastle	Tesoro Petroleum Corp.	Thermofofor	4,000	7,000
Casper	Texaco, Inc.	Fluid	7,000 ¹	7,000 ^{1, 2}

TABLE I-2

U.S. FLUID CATALYTIC CRACKING CAPACITY BY PAD

(Fresh Feed and Recycle)

<u>PAD District</u>		<u>Fresh Feed (BPSD)</u>	<u>Fresh Feed & Recycle (BPSD)</u>		<u>Percent of Total</u>
1	Delaware	(62,000)	77,000		
	New Jersey	(229,444)	269,444		
	New York	(41,000)	47,000		
	Pennsylvania	(206,000)	224,300		
	Virginia	(27,000)	32,000		
	Total	(565,444)		649,744	12
2	Illinois	(429,277)	523,277		
	Indiana	(193,000)	203,800		
	Kansas	(163,700)	206,450		
	Kentucky	(54,000)	55,000		
	Michigan	(39,500)	46,900		
	Minnesota	(71,500)	74,500		
	Missouri	(41,000)	53,000		
	Nebraska	(2,400)	2,900		
	North Dakota	(23,000)	34,000		
	Ohio	(202,460)	248,500		
	Oklahoma	(191,200)	231,675		
	Tennessee	(13,500)	13,500		
	Wisconsin	(9,700)	10,700		
	Total	(1,434,237)		1,704,202	30
3	Arkansas	(15,000)	18,000		
	Louisiana	(617,778)	677,728		
	Mississippi	(70,500)	76,850		
	New Mexico	(12,400)	17,560		
	Texas	(1,257,166)	1,527,571		
	Total	(1,972,844)		2,317,709	41
4	Colorado	(22,500)	23,900		
	Montana	(46,300)	72,500		
	Utah	(53,600)	70,160		
	Wyoming	(58,778)	74,078		
	Total	(181,178)		240,638	4

Table I-2 cont'd

U.S. FLUID CATALYTIC CRACKING CAPACITY BY PAD

<u>PAD District</u>		<u>Fresh Feed (BPSD)</u>	<u>Fresh Feed & Recycle (BPSD)</u>	<u>Percent of Total</u>
5	California	(485,611)	621,211	
	Hawaii	(14,100)	23,000	
	Washington	(91,500)	<u>118,600</u>	
	Total	<u>(591,211)</u>	<u>762,811</u>	13
U.S. TOTAL		(4,744,914)	5,675,104	

Source: The Oil and Gas Journal, March 29, 1976.

PETROLEUM ADMINISTRATION FOR DEFENSE (PAD) DISTRICTS

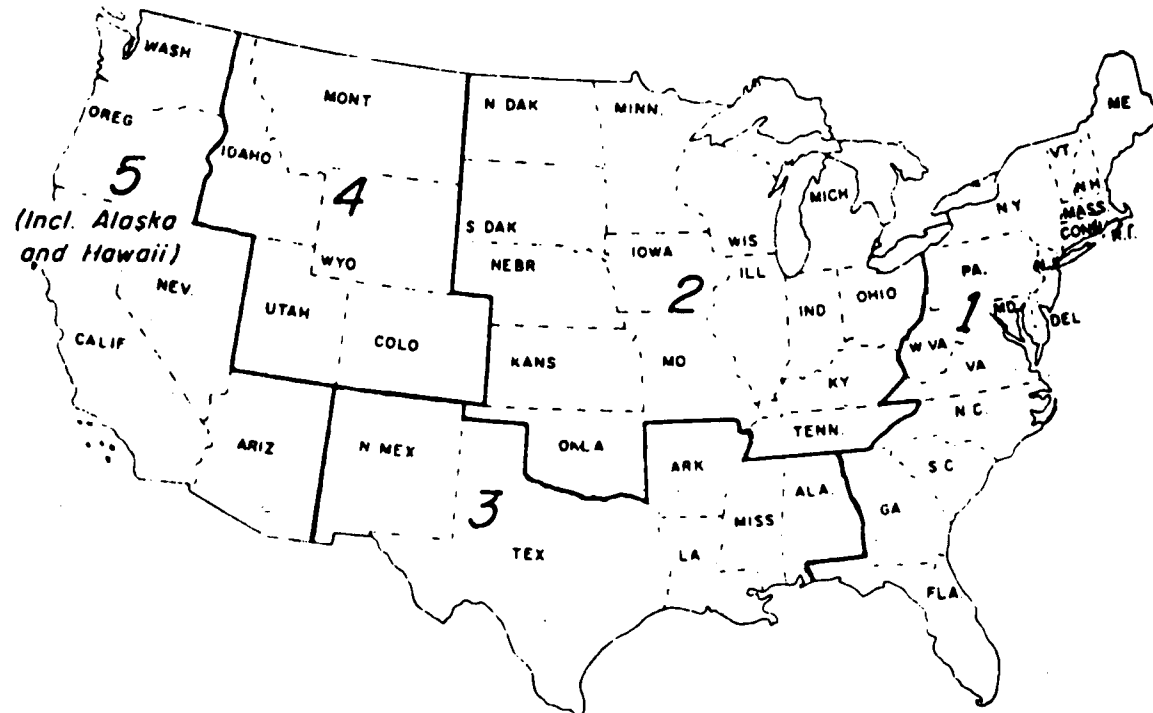


FIGURE I-1

TABLE I-3

CAPACITY OF REFINERIES WITH FCC REGENERATORS
USING HYDROTREATING

	<u>Fresh Feed (BPSD)</u>	<u>Approximate % of Total</u>
<u>PAD 1</u>		
New York	20,000	
Pennsylvania	<u>40,000</u>	
Total	60,000	10
<u>PAD 2</u>		
Illinois	27,000	
Michigan	12,500	
Minnesota	20,000	
Ohio	<u>22,500</u>	
Total	82,000	4
<u>PAD 3</u>		
Louisiana	41,000	
Mississippi	23,000	
Texas	<u>70,000*</u>	
Total	134,000	6
<u>PAD 4</u>		
Wyoming	<u>16,000</u>	
Total	16,000	7
<u>PAD 5</u>		
California	58,000	
Washington	<u>8,500</u>	
Total	<u>76,500</u>	10
GRAND TOTAL	368,500	6**

**6,000 BPD listed as cat cracker and cycle stock feed pretreatment and middle distillate.

**Percent of total U.S. capacity.

Source: The Oil & Gas Journal, March 29, 1976.

In undertaking this study we also investigated what fraction of the population have carbon monoxide (CO) boilers. Data available from the National Emission Data System (see Table I-4) shows 31 facilities with 28% of fresh feed capacity have CO boilers. However, conversations with state and local environmental control agencies and others (documented in Appendix C) have led us to believe that the figure is closer to 60-70% of total capacity.

The current technology advance being applied to FCC units is the application of high temperature regeneration (HTR) or in-situ CO combustion. The application of this technology improved catalyst regeneration and reduces CO emissions. Based on interviews with industry representatives (Appendix C), it is estimated that about 15% of U.S. catalytic cracking capacity is based on HTR.

FCC units represent a large investment and are normally operated at full capacity. Run periods for FCC units typically last three to four years, after which the unit is shut down for repairs and maintenance. On the average, the repair and maintenance period is about one month. Thus, the normal fractional utilization of existing capacity can be assumed at 97%. Run lengths of six years without shutdown have been achieved.

C. GROWTH PROJECTIONS

Projecting growth rates for the petroleum industry is extremely difficult at present due to the ambiguity of government environmental and energy policies. In addition, new refining facilities require enormous capital investments which are being deferred until future requirements are better defined.

The growth of FCC capacity is particularly affected by these uncertainties because it is a key process for production of both motor and middle distillate (heating and diesel) fuels. The FCC process has a certain amount of inherent flexibility which permits optimization of the yields to match product demands for these fuels. Therefore, FCC capacity is tied directly to the growth projections for gasoline and middle distillate.

Current U.S. fluid catalytic cracking capacity (fresh feed) is 4,745 K BPSD based on the latest Oil and Gas Journal Annual Refining Survey.⁹ Planned additions to capacity, all of which will be completed by 1976, amount to 81.5 K BPSD or about 1.7% of 1975 capacity (see Table I-5). There are no domestic FCC construction projects beyond 1976 indicated in the recent Oil and Gas Journal worldwide construction survey.¹²

As indicated earlier, gasoline demand is an important factor effecting expansion of FCC capacity. Cantwell¹¹ of DuPont recently presented gasoline demand projections at the API meeting in Los Angeles. Two scenarios were presented:

Scenario 1: Gasoline growth of 1.5% per year through 1980, peaking in 1980 at 8% above 1975 level and then declining at 1.6% per year back to 1975 level in 1985.

TABLE I-4

FCC'S WITH CO BOILERS*

	<u>State</u>	<u>Operator</u>	<u>Location</u>
1	California	Atlantic Richfield	Carson Pt 17
	California	Atlantic Richfield	Carson Pt 18
2	California	Gulf Oil Corp.	Santa Fe Springs
3	California	Mobil Oil Corp.	Torrance
4	California	Powerline Oil Co.	Santa Fe Springs
5	California	Standard Oil of California	El Segundo
6	California	Texaco, Inc.	Wilmington
7	California	Union Oil Co. of California	Los Angeles
8	California	Shell Oil Co.	Wilmington (Carson)
9	California	Exxon Co., USA	Benicia
10	Delaware	Getty Oil Co.	Delaware City
11	Hawaii	Standard Oil of California	Barbus Point
12	Illinois	Texaco, Inc.	Lawrenceville (St. Lawrence Fld.)
13	Kansas	Petrofina Co.	El Dorado
14	Kansas	Skelly Oil Co.	El Dorado
15	Kansas	Apco Oil Corp.	Arkansas City
16	Kansas	National Co-op Refinery Association	McPherson
17	Kansas	CRA, Inc.	Coffeyville
18	Kansas	CRA, Inc.	Phillipsburg
19	Kansas	Phillips Petroleum	Kansas City
20	Kentucky	Ashland Oil Co.	Catlettsburg (Leach)
21	Louisiana	Exxon Co., USA	Baton Rouge
22	Louisiana	Shell Oil Co.	Norco
23	Montana	Exxon Co., USA	Billings
24	New Jersey	Exxon Co., USA	Linden
25	Ohio	Ashland Petroleum Co.	Canton
26	Oklahoma	Vickers Petroleum Corp.	Ardmore
27	Texas	Shell Oil Co.	Deer Park
28	Texas	Exxon Co., USA	Baytown
29	Utah	Caribiou (Phillips)	Woods Cross
30	Utah	Chevron Oil Co.	Salt Lake City
31	Utah	Amoco	Salt Lake City

*Partial listing.

Source: National Emission Data System Point Source Listing (latest update of data ranges from 1970-1974).

TABLE I-5
FCC EXPANSIONS
(Fresh Feed)

<u>Company and Location</u>	<u>Net Capacity Addition (BPSD)</u>	<u>Capacity Before Expansion (BPSD)</u>	<u>Year of Completion</u>
Champlin Petroleum Co. Corpus Christi, Texas	41,000	10,000	1976
Charter International Oil Houston, Texas	26,000	24,000	1976
Exxon Co., USA Baytown, Texas	5,000	124,000	1976
Good Hope Refineries Louisiana	<u>9,500*</u>	15,000	1976
Total Additions	81,500		

*16,000 BPSD expansion to 24,500 BPSD total capacity. Net addition is
24,500 - 15,000 = 9,500 BPSD.

Source: The Oil and Gas Journal, Construction Survey, 1976.

Scenario 2: Gasoline growth of 2.3% per year peaking in 1981 at 15% above 1975 level and then declining at 1.6% per year to 8% above 1975 level by 1985.

Scenario 1 assumes that small cars will increase their market share from 50 to 60% by 1980, that vehicle miles per car will remain constant and that fuel economy will improve as required by EPA. Scenario 2 presumes consumer resistance to small cars and only partial achievement of fuel economy goals.

The average compound growth rate over the ten year period is about 3/4% per year for scenario 2. The growth rate of FCC capacity over this same period is projected at 1/2% per year by one of the process licensors (see Appendix C). A catalyst supplier we contacted forecasts FCC growth at about 2% per year through 1980 and probably tapering off after that.

Using this information, we adopted the following growth projection as a basis for the impact calculations.

PROJECTED GROWTH OF FCC CAPACITY

1.5% per year through 1980

0% per year through 1985

This is an average compound growth over 10 years of about 3/4%. The initial growth is also about the same as from 1975 to 1976.

It is most probable that some of this additional capacity will be obtained through modification of existing units to remove bottlenecks or to improve yields by applying HTR or feed hydrotreating. However, since the overall growth projections are very modest, we have assumed for the purpose of calculating the impact of NSPS, that the additional capacity would come from new units. The impact under this assumption will represent a maximum benefit case.

For the purpose applying the Model IV calculation procedure, the following growth or conversion to HTR was assumed.

<u>Year</u>	<u>HTR, % of Fresh Feed Capacity</u>
1975	15
1978	25
1980	33
1985	60

D. SULFUR CONTENT OF FCC FEED

In order to calculate present and future SO_x emissions nationwide, it was necessary to estimate the average sulfur content of current and projected FCC feeds. This was done by PAD district, excluding PAD District IV, where the refining capacity is insignificant. PAD District II is subdivided into large and small refinery operations for better characterization of the industry. Likewise PAD III is characterized by the two large refining states contained in the district.

Typical crude slates for the years 1977, 1980, and 1985 have been established previously for EPA by ADL.¹³ The general objective in selecting crude slates for each district was to simulate as closely as possible the average mixture of crudes which would be run in each refining area in a given year. Specifically, the crude slates were chosen to simulate the average domestic/foreign mix, the sulfur content, the API gravity, and other key properties. The crude slates are shown by PAD district in Table I-6.

Also shown in Table I-6 is the average sulfur content of FCC feeds in future years. These sulfur levels were estimated using the yield data in Table I-7 and assuming that the fresh catalytic cracker feed was composed of both heavy gas oil and vacuum gas oil; i.e., everything in the boiling range 500-1050°F. For determining the feed sulfur content, this is a good approximation. The sulfur levels in Table I-6 do not take into consideration hydrotreated feedstocks. This is considered in Chapter V.

The sulfur content of FCC feeds is shown to increase with time in PAD Districts I and II due to increased use of foreign high sulfur crudes. In PAD V there is a slight decline in sulfur content after 1977 showing the effect of Alaskan crude which is slightly lower in sulfur than crudes presently processed. These trends were taken into account in the development of emission baselines and uncontrolled emission levels which are discussed in Chapter V.

TABLE I-6

SIMULATED CRUDE SLATES AND FCC FEED SULFUR CONTENT

	Pad District	Crude Type	Crude (vol. %)				Average Wt. % S in Catalytic Cracker Feed			
			73	77	80	85	73	77	80	85
I	East Coast	L	15.4	--	--	--				
		T	7.6	--	--	--				
		N	16.2	17.2	18.2	19.2	0.82	1.13	1.16	1.19
		A	7.6	35.7	40.7	45.7				
		V	31.7	26.5	21.5	16.5				
		AL	21.5	20.6	19.6	18.6				
II	Midwest - Small (Okla., Kan., etc.)	L	7.6	6.0	2.9	--				
		T	13.1	12.0	10.9	10.0				
		O	61.5	59.8	58.0	55.8				
		MC	17.8	8.8	--	--	0.47	0.53	0.60	0.64
		A	--	6.7	14.1	17.1				
		AL	--	6.7	14.1	17.1				
	Midwest - Large (Ill., Ind., etc.)	L	6.0	2.9	--	--				
		T	70.3	63.8	60.1	55.1				
		O	4.9	4.7	4.6	4.4	1.42	1.56	1.69	1.70
		A	8.5	23.5	35.3	40.5				
		MC	10.3	5.1	--	--				
III	Louisiana Gulf	L	88.7	88.2	88.2	88.2				
		T	11.3	11.8	11.8	11.8	0.40	0.41	0.41	0.41
	Texas Gulf	L	47.4	47.4	47.4	47.4				
		T	41.4	41.4	41.4	41.4				
		N	3.8	3.8	3.8	3.8	1.54	1.54	1.54	1.54
		A	5.3	5.3	5.3	5.3				
		V	2.1	2.1	2.1	2.1				
	West Coast	CW	37.4	40.0	40.0	40.0				
		CV	13.8	13.2	13.2	13.2				
		A	31.3	33.4	--	--	1.31	1.35	1.09	1.09
		MC	7.1	3.4	--	--				
		I	10.4	10.0	--	--				
		ANS	--	--	46.8	46.8				

LEGEND: L = Louisiana
T = West Texas Sour
O = Oklahoma
CW = California Wilmington

CV = California Ventura
ANS = Alaskan North Slope
N = Nigerian Forcados
A = Arabian Light

V = Venezuelan Tia Juana
AL = Algerian Hassi Messaoud
MC = Mixed Canadian
I = Indonesian Minas

TABLE I-7

GAS OIL YIELDS AND SULFUR CONTENT

<u>Crude</u>	<u>Yield of Heavy Gas Oil (500-650°F) (Vol. %)</u>	<u>Yield of Vacuum Gas Oil (650-1050°F) (Vol. %)</u>	<u>Wt. % S in H.G.O.</u>	<u>Wt. % S in V.G.O.</u>
Louisiana	19.50	32.50	0.0901	0.3221
West Texas Sour	14.11	29.60	1.2187	1.8513
Oklahoma	11.77	28.04	0.1296	0.2327
California Wilmington	11.96	38.54	0.9124	1.3126
California Ventura	12.53	32.08	1.1393	1.5411
Alaskan North Slope	15.50	29.49	0.4547	1.1029
Nigerian Forcados	20.60	30.40	0.2015	0.3125
Arabian Light	15.01	29.50	1.0807	2.3215
Venezuelan Tia Juana	12.70	32.80	0.6690	1.6292
Algerian Hassi Messaoud	11.92	22.71	0.0756	0.2249
Mixed Canadian	15.20	25.60	0.4362	0.7121
Indonesian Minas	15.00	41.00	0.0361	0.0890

Source: Refinery Model Study, Appendix H, "The Impact of Lead Additive Regulations on the Petroleum Refining Industry," by Arthur D. Little, Inc., EPA Contract 68-02-1332, Task Order 7, December 1975.

II. SOURCES AND TYPES OF EMISSIONS

There are six different licensors of FCC technology. However, since catalytic cracking has been an important commercial process for over thirty years, the various processes have evolved toward each other. Design differences among the processes do not affect the character of the emissions from catalyst regeneration. Therefore, FCC technology with conventional regeneration is treated for purposes of this study as though there were only one licensor.

A. PROCESS DESCRIPTION

Figure II-1 is a schematic flow diagram of a typical fluid catalytic cracking process. The major pieces of equipment are the regenerator, the riser cracker, the catalyst separator, and the fractionator. Fresh feed is mixed with recycle from the fractionator before entering the riser cracker, where the bulk of the cracking reactions occur. The riser cracker is designed for plug flow (i.e., the catalyst is entrained in the oil vapors) to maximize the catalyst activity and selectivity, since the amount of carbon-on-catalyst is the smallest at the bottom. Hence, the term "fluid" catalytic cracking is a misnomer in that the cracking no longer takes place within a fluid bed. The substitution of riser cracking for fluid beds was initiated by the introduction of the highly active zeolite catalysts, which reduce the required cracking time to a few seconds.

The catalyst separator is designed to disengage the catalyst and cracked products as rapidly as possible to avoid subsequent cracking. Internal cyclones remove some of the catalyst fines from the product vapors. The product vapors travel overhead to the fractionator. Essentially all the entrained catalyst fines exit in the column bottoms stream, which ultimately goes to a settler. A catalyst sludge is removed from the settler and is mixed with the liquid recycle for reinjection into the riser reactor.

In the separator, the catalyst, now containing deposited coke, falls through a steam stripping section, where residual heavy oil is removed. The catalyst activity is restored by burning off the carbon in the regenerator, with air. The combustion gases exit the regeneration through internal cyclones which recover catalyst fines. The regenerator flue gas may then be routed to an electrostatic precipitator and/or a CO boiler.

The only source of airborne emissions from the process is the flue gas, which may contain CO, SO₂, SO₃, hydrocarbons, NO_x and particulates. Hence, the remainder of the discussion will be limited to catalyst regeneration.

B. REGENERATION

There are basically two types of regeneration: (a) traditional and (b) complete CO combustion, otherwise known as high-temperature regeneration (HTR). HTR is a relatively recent innovation, and, consequently it

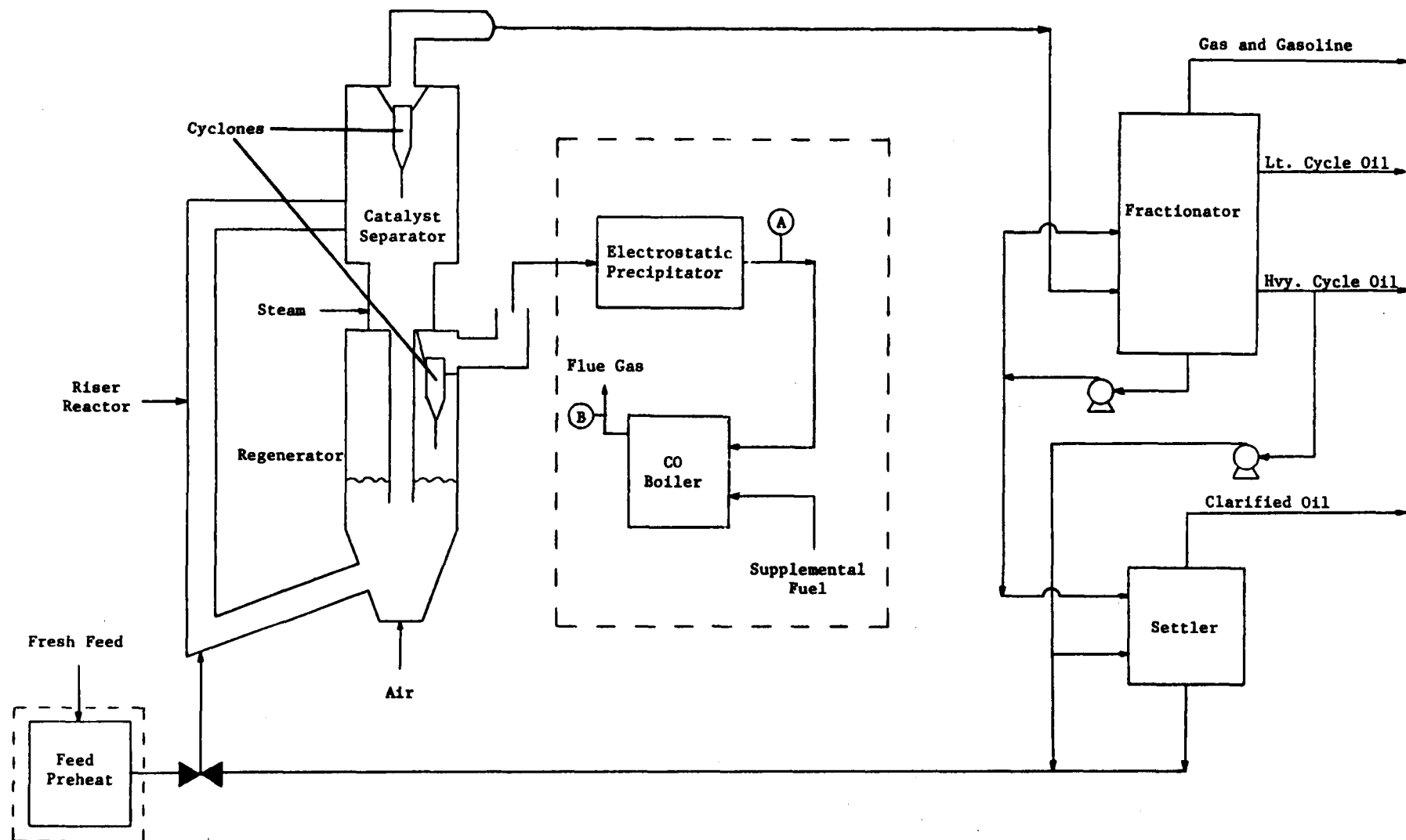


FIGURE II-1 TYPICAL FLUID CATALYTIC CRACKING UNIT

is used in a minority of FCC units. HTR offers significant advantages over traditional regeneration, most of them directly affecting the emissions. These advantages are as follows:

1. More complete catalyst regeneration. Both the catalyst activity and selectivity are improved; less coke is produced per unit of feed, which reduces the SO_x emissions, because the sulfur on the catalyst going to the regenerator is related to the carbon on the catalyst.
2. Lower catalyst inventory. The complete regeneration increases the catalyst activity, which means that a lower catalyst-to-oil ratio is possible. In turn, the unit's capacity or severity can be increased if bottlenecks are removed from the rest of the process.
3. Better heat recovery within the regenerator. The major oxidation reactions are as follows:

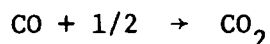
<u>Reaction</u>	<u>Heat Released (Btu/lb carbon)</u>
$\text{C} + 1/2 \text{O}_2 \rightarrow \text{CO}$	4,440
$\text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2$	10,160
<hr/>	<hr/>
$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	14,160

Traditional regenerators do not allow complete CO oxidation, and, hence, a large quantity of heat is either lost or must be recovered in a CO boiler.

4. Low CO emissions. It is possible to meet the 500 ppm CO NSPS without a CO boiler.

Due to these advantages, some "traditional" units have been revamped for high-temperature regeneration. Generally, revamping requires the replacement of cyclones, the plenum chamber, cyclone diplegs, the regenerator grid and seals, and the catalyst overflow weir, all of which must be type 304 stainless steel rather than carbon steel in order to withstand the higher temperatures, resulting from HTR.

Essentially complete catalyst regeneration at lower temperatures can be achieved through the use of CO oxidation promoter catalysts. These catalysts are identical in terms of cracking performance to their non-promoter counterparts, however, they contain metals which catalyze the regenerator reaction



Hence, a lower regenerator temperature can be used to meet the CO NSPS without upgrading the metallurgy of the regenerator internals for HTR. The promoter catalysts are considerably more expensive, however, which means that there is a tradeoff between capital expenditure and increased catalyst cost. The SO_x emissions from a process using the promoter catalyst would be greater than the HTR case at the same cracking conditions. Regeneration of the catalyst is not quite as effective at the lower temperature; hence, the selectivity of the catalyst is slightly poorer in that more coke is produced.

C. CONDITIONS

Table II-1 lists the ranges of conditions for the FCC process including both traditional and high-temperature regeneration. Processes using a promoter catalyst would have a regeneration temperature typically in the range of 1160-1200°F.

Yields

Expected yields vary considerably with feedstock for the three generic categories of feedstocks--aromatic, naphthenic, and paraffinic as indicated in Table II-2. Generally, the highest conversions (conversion is defined as 100 minus percent cycle oil) are obtained from paraffins and the lowest from aromatics, which are more refractory. Most of the difference in yield structure between paraffins and naphthenes lies in the higher gas make for the former.¹⁴

The concentration of aromatic molecules determines the coke yield, and, hence, is important with regard to emissions. Hydrotreating the feed can convert some of the aromatics to naphthenes, thereby reducing the coke make and increasing the conversion. In fact, it has been shown that hydrotreating catalyst cracker feed to increase the conversion can be economically attractive in certain cases.¹⁵

D. EMISSIONS FROM A TYPICAL FCC UNIT

The major source of airborne emissions (exclusive of fugitive emissions) in an FCC unit is the regenerator flue gas. As shown in Figure II-1, this gas may be routed through an electrostatic precipitator and/or a CO boiler; the order of the precipitator and boiler may also be reversed. In addition, there may be a heat recovery unit downstream of the regenerator (not shown).

In Table II-3, emissions for a typical FCC unit are summarized. Point A lies between the electrostatic precipitator and the CO boiler; typical emissions for both types of regeneration are indicated. Point B lies downstream of the CO boiler; only the traditional regeneration case is considered at this point, since it is assumed that high-temperature regeneration is sufficient for meeting the CO NSPS. It should be noted, however, that the use of HTR does not necessarily preclude the use of CO boilers. Some refiners (Exxon, for instance) prefer to use medium-temperature regeneration to obtain the benefits from improved catalyst selectivity without

TABLE II-1

RANGE OF CONDITIONS FOR FLUID CATALYTIC CRACKINGReactor

Temperature, °F	885-1025
Pressure, psig	9-40
Catalyst/Oil Ratio (wt.)	3-20
Riser Velocity, ft/sec	15-70
Coke Content of Spent Catalyst, wt. %	0.25-6
Recycle Ratio, % Recycle to Fresh Feed	0-100

Regenerator

Temperature, °F - Traditional Regeneration	1000-1100
- HTR	1100-1350
Pressure, psig	9-40
Coke Content of Regenerated Catalyst, wt. %	0.05-1.0

TABLE II-2

TYPICAL PRODUCT DISTRIBUTIONS

<u>Feedstock Description</u>	<u>Aromatic</u>	<u>Naphthenic</u>	<u>Paraffinic</u>
Conversion, vol. % ¹	70	85	93
Yields, vol. %			
Gasoline, C ₅ -430°F. TBP ep	54.2	70.0	73.0
Butane-butene	16.8	19.0	22.5
isobutane	5.9	7.3	8.0
n-butane	1.4	1.9	2.5
butenes	9.5	9.8	12.0
Propane-propylene	7.5	8.5	12.0
propane	2.0	2.4	3.3
propylene	5.5	6.1	8.7
Light cat gas oil	20.0	10.0	5.0
Decanted oil	10.0	5.0	2.0
Total	108.5	112.5	114.5
Coke, wt. %	6.3	5.4	4.8
C ₂ and lighter, wt. %	3.0	2.8	2.5
H ₂ S, wt. %	0.4	0.2	0.1

Source: The Oil and Gas Journal - October 30, 1972

¹Conversion defined as 100 minus percent cycle oil.

TABLE II-3

CURRENT EMISSION RATE FROM TYPICAL FCC UNIT

Capacity - 50,000 BPSD

Significant Emission Sources	Gas Volume	Gas Composition - ppm						Pollutant Emission				
		(Wet Basis Except for Particulates)						Rate-lb/hr				
	SCFM	Part. gr/dscf	SO _x ¹	NO _x ²	CO	HC	O ₂	Part.	SO _x	NO _x	CO	HC
<u>POINT A</u> ³												
Traditional Regeneration	87,050 (4.3% H ₂ O)	0.055	1,360	200	114,000	500	N11	39.4	1,200	127	44,000	110.3
High-Temperature Regeneration	92,500 (3.4% H ₂)	0.043	1,070	200	500	10	9,800	32.8	1,000	134.4	205.0	2.3
<u>POINT B</u> ⁴												
Traditional Regeneration	110,950	0.043	1,070	200	10	10	10,000	39.4	1,200	162	4.9	2.8
	110,950	0.043	1,070	200	10	10	10,000	39.4	1,200	162	4.9	2.8

See Text for Discussion of Data Sources and Assumptions

¹Expressed as SO₂²Expressed as NO₂³lies between electrostatic precipitator and CO boiler⁴lies downstream of CO boiler

requiring the replacement of the regenerator internals. In this regard, the cases in Table II-3 can be considered extremes, and the emissions for the typical medium-temperature case would be somewhere in-between.

The sources of the emission data in Table II-3 are discussed below.

1. Gas Volume

For the calculation of gas volume, a typical coke composition was assumed. The appropriate chemical equations for the regenerator reactions were written and from these the gas volume was calculated for each case. A sample calculation is given in Appendix A. The assumptions were as follows:

- The coke composition is 96% C, 3% H, 1% S
- The coke yields were as follows:¹⁶

Traditional regeneration - 6% by weight of feed

High-temperature regeneration - 5.0% by weight of feed

- The CO₂/CO mol ratio leaving the regenerator is 1.0 for traditional regeneration; only CO₂ leaves the regenerator for the HTR case.
- For the CO boiler and for HTR, the excess air was assumed to be 5%.¹⁰
- It was assumed that the CO boiler did not use auxiliary fuel.

2. Particulates

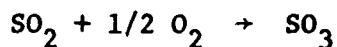
Particulate emissions are restricted by an NSPS to 1 kg particulates per 1000 kg coke burn-off so this was used as a typical emissions level. To calculate the particulate emissions, it was assumed that the coke yields were as shown above. The gas volume calculated for part 1 were used to determine the concentrations.

3. SO_x

SO_x emissions vary widely, depending primarily upon the cracking conditions and the feedstock quality (discussed in Chapter I). Since essentially all the carbon is removed from the catalyst by regeneration, all the sulfur contained in the coke is converted to SO_x and is emitted with the flue gas. The typical SO_x emissions shown in Table II-3 were calculated as follows. The average rate of SO_x emissions (per barrel of fresh feed) in the United States for 1978 was estimated (see Chapter V) and scaled up to 50,000 BPSD, the result being 1,200 lb/hr as indicated for the two traditional regeneration points in Table II-3. For the same cracking conditions, HTR reduces the coke production--typically to 5.0 wt. %

of fresh feed for HTR from 6.0% for traditional regeneration.¹⁶ Since the SO_x emissions are roughly proportional to the coke make, the emission rate for the HTR case was scaled down by 5.0/6.0 ratio. The gas concentrations were calculated assuming 1) gas volumes as shown in Table II-3, 2) SO_x as SO₂, and 3) regenerator off-gas molecular weight, 29.

It has been found by several groups that a portion of the SO_x is present as SO₃, apparently formed by the reaction equals



There is disagreement as to the percentage of SO_x as SO₃; estimates have ranged from 0.1-60%. Amoco indicated that concentrations of SO₃ well in excess of the calculated equilibrium value for the reaction above under the regenerator conditions have been observed. However, this phenomenon is presently unexplainable. Exxon stated that the SO₃/SO₂ ratio is generally 0.03 from their units. Clearly, more data are needed since a high SO₃ concentration could have a large impact on the operation of certain scrubber systems.

4. NO_x

Very few data are available on NO_x emissions. The Monsanto Report summarized data from previous studies and the range of emissions downstream of a traditional regenerator was 8-394 ppm. Downstream of the CO boiler it was 0-500 ppm. Interviews with Exxon and Amoco provided the following estimates:

	After HTR (ppm NO _x)	After CO Boiler (ppm NO _x)
Exxon	<200	<200
Amoco	5-20	<50

It was assumed that a typical NO_x emission was 200 ppm for each case. However, there is obviously a paucity of useful data. In addition, the data for emissions downstream of the CO boiler are probably biased upward due to the common practice of burning supplemental fuel in the boiler.

In general, one would expect the NO_x emissions from HTR to be lower than those from a CO boiler due to the lower temperature; this is indicated by the Amoco figures.

5. Carbon Monoxide

Carbon monoxide emissions are now restricted to 500 ppm by a NSPS. The standard was set to allow HTR units to meet the standard without a CO boiler. Hence, 500 ppm was chosen as a typical emission level from high-temperature regeneration.

The CO level between a traditional regenerator and the CO boiler was calculated by stoichiometry using the assumptions in part 1.

The emission level downstream of the CO boiler was estimated from actual stack sampling data.¹⁷ For five cases, the CO concentrations were 0, 0, 5, 10, and 25 ppm; the average is approximately 10 ppm, so this figure was assumed for Table II-3.

6. Hydrocarbons

The level of hydrocarbon emissions is very low. Interviews with Amoco and Exxon produced the following estimates:

	<u>After HTR</u>	<u>After CO Boiler</u>
Exxon	<5 (non-methane)	--
Amoco	<10	<10

UOP reasoned that hydrocarbon emissions are practically nil because the combustion reactions in a boiler or in a regenerator are rate-limited by the combustion of carbon monoxide--not by the combustion of hydrocarbons.

P.O.M.'s or P.N.A's

Importance is attached to the polynuclear aromatics in the hydrocarbons due to their potential carcinogenic effect. The P.N.A. present in significant quantity in FCC flue gas is Benzo-A-Pyrene (BAP). The concentration of BAP in the flue gas from conventional regenerator is 0.481 lbs/1,000 barrels.¹⁸ The BAP concentration is effectively reduced in the CO boiler. The concentration of BAP in the flue gas from CO boilers is 0.031×10^{-3} lb/1,000 barrels. It is expected that the BAP concentration from the HTR units is comparable to the BAP concentration in the CO boiler flue gas; however, there is no data to establish this as fact.

7. Oxygen

Downstream of a traditional regenerator, the oxygen concentration is insignificant because less-than-stoichiometric air is supplied. For the two remaining cases, the oxygen in the stack is set entirely by the excess air supplied, and is about 10,000 ppm in each case here (5% excess air).

E. FACTORS AFFECTING SO_x EMISSIONS

This discussion is confined to SO_x emissions, since other species are of lesser importance in terms of the impact of NSPS (see Chapter III).

The two most important parameters affecting SO_x emissions are the coke yield and the feed sulfur content. The coke yield is important since all the sulfur in the coke is ultimately discharged as SO_x. The feed sulfur content is significant since there appears to be a correlation between

feed sulfur content and coke sulfur content, though the relationship is not well understood.

Since high-temperature regeneration (HTR) produces a more selective catalyst, coke make is 20-30% lower than that for traditional regeneration. Hence, HTR units create smaller SO_x emissions. Other than the type of regeneration, the parameters affecting coke yield are feed type (discussed earlier) and the severity of operating conditions. Since heavier feeds produce more coke, coke production is expected to increase in this country as heavier foreign crudes are substituted for domestic crudes.

There are two published articles^{19, 20} on the subject of sulfur distribution in catalytic cracking; they are in general disagreement in their attempts to correlate coke sulfur content with the feed sulfur content. Data from Amoco are presented as a plot of the ratio (wt. % sulfur in coke)/(wt. % sulfur in feed) versus conversion (see Figure II-2). The result is a series of parallel lines with small slope; the sensitivity to conversion is smaller than expected. The ratio of sulfur in coke to sulfur in feed varies from about 0.5-0.8 for virgin (unhydrotreated) feeds and from approximately 0.3-0.6 for the same feedstocks, but hydrotreated. It is surprising that the ratio would be lower for the hydrotreated feedstocks since hydrotreating does not remove much of the multi-ring thiophenes, which are the species expected to remain in the coke. The Amoco authors concluded that there is "no clear correlating parameter using the sulfur-type analysis." However, it was stated that this may be due to the uncertainty created by the large number of unanalyzed sulfur compounds.

A separate article by Gulf²⁰ (see Figure II-3) indicates that the above ratio is 2-3 for low-sulfur feeds--obtained by hydrotreating higher-sulfur feeds--and 1-2 for the unhydrotreated stocks. These data are directly opposite from the Amoco data. The Gulf authors imply that there is a correlation between feed sulfur type and coke sulfur content. The Gulf data are indirectly supported by a Chevron paper²¹.

Although one would expect a correlation between feed sulfur content and coke sulfur content, the relationship has not been adequately developed. Nevertheless, it can be said that, the higher the feed sulfur, the higher the coke sulfur and, consequently, the higher the SO_x emissions. As the heavier and more sour foreign crudes are substituted for domestic crudes, increases in SO_x emissions are expected nationwide.

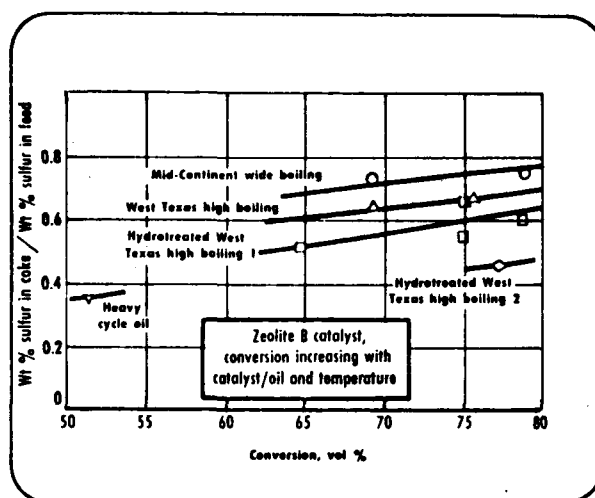


FIGURE II-2 FEED TYPE AND COKE SULFUR LEVEL

Source: Wollaston, E.G., "Sulfur Distribution in FCU Products," The Oil and Gas Journal, August 2, 1971.

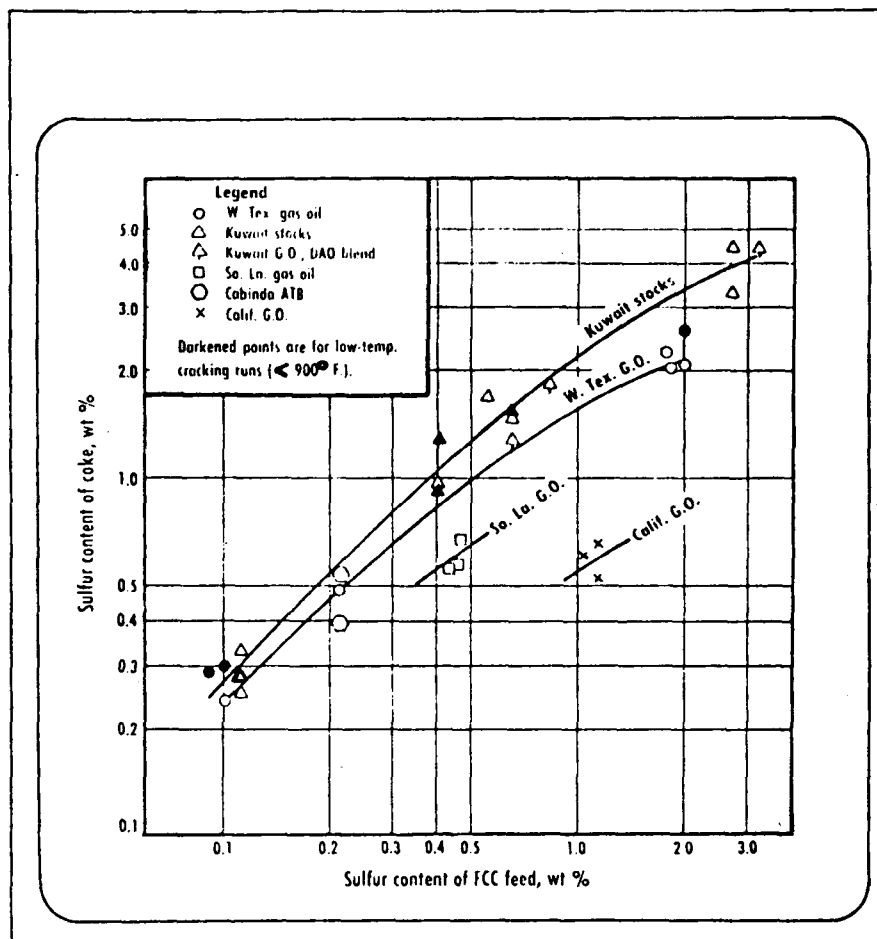


Figure II-3 Sulfur Content of Coke

Source: Huling, G.P., J.D. McKinney, and T.C. Readal, "Feed Sulfur Distribution in FCC Product," The Oil and Gas Journal, May 19, 1975.

III. BEST APPLICABLE SYSTEMS OF EMISSION REDUCTION

The emissions from FCC regenerators and the factors that affect emissions were described in the previous chapter. The pollutants include particulates, CO, SO_x, NO_x and hydrocarbons. In this chapter, the control technology to reduce the pollutant emissions is discussed. This information may be used in the establishment of New Source Performance Standards (NSPS).

At present, NSPS are implemented for particulates and CO; therefore, control technology for these pollutants is not discussed here. A discussion of NO_x control technology is also omitted, since SO_x and hydrocarbons are of primary concern. Pollution control technology for SO_x and hydrocarbons is well-developed and the majority of this chapter is devoted to describing control systems for these pollutants. The control status of all the pollutants is briefly discussed first.

A. CONTROL STATUS

1. Particulates

The existing NSPS for particulate emissions is 1 kg/1,000 kg of coke burned, or about 0.038 gr/scfd. This control level can be achieved during the FCC on-stream period by well-maintained cyclones followed by an electrostatic precipitator. Hence, the present control level is consistent with best available technology.

The current control level may be slightly beyond the capability of low-energy wet scrubbers. It is necessary to use a medium- or high-energy scrubber to meet NSPS for particulates.

2. Carbon Monoxide

The existing NSPS for carbon monoxide in FCC regenerator flue gases is 500 vppm. This level was established based on data provided by Amoco that demonstrated that high-temperature regeneration could reduce the CO emission below 500 ppm. Carbon monoxide emissions after CO boilers are generally less than 50 ppm¹⁷ and many new units without HTR would likely include CO boilers to increase the total energy efficiency of the refinery. However, purchasers of new FCC units would also consider the benefits of yield improvements and lower capital costs (no CO boiler) associated with HTR. If the NSPS on CO were reduced below 500 ppm, this latter option of HTR would be eliminated due to non-compliance. A rational basis was used to set the existing NSPS on CO and the logic still applies.

3. Oxides of Nitrogen

There is no NSPS for NO_x emissions from FCC regenerators. NO_x emissions are generally less than 200 ppm after the CO boiler and in the flue

gas from HTR, according to information obtained from interviews with industry representatives.

<u>Source</u>	<u>NO_x EMISSION</u>	
	<u>Ex. HTR</u>	<u>Ex. CO Boiler</u>
Exxon R&E	<200 ppm	<200 ppm
Amoco	5-20 ppm	<50 ppm

It appears that in some cases the concentrations are relatively low.

Even if the concentration was of potential concern, effective control technology for NO_x is still being developed. The enforcement of an NSPS for this pollutant would, therefore, have to await commercialization of control technology.

4. Hydrocarbons

The hydrocarbon emissions depend on the type of regeneration (high-or-low-temperature). Also, CO boilers effectively reduce or even eliminate the hydrocarbon emissions. The hydrocarbon emissions in the FCC flue gas at various locations are given as below.

<u>Source</u>	<u>Hydrocarbon Emissions in Flue Gas, ppm</u>
Conventional Regenerator	<500
CO Boiler	<10
High Temperature Regenerator, HTR	<10

The NSPS only apply to new and modified sources. At present, a NSPS to control hydrocarbon emissions does not exist. It is expected that new or modified FCC's will utilize HTR or have CO boilers, therefore, a NSPS would have a minimal effect on the control of hydrocarbon emissions from FCC's. In effect, the NSPS for CO has simultaneously controlled the emission of hydrocarbons to relatively low levels. The effect of a possible NSPS standard for hydrocarbons is shown in Chapter V.

The control technologies to reduce hydrocarbon emissions are HTR or use of a CO boiler. Since HTR is discussed in the previous chapter and the petroleum industry is familiar with CO boilers, control technology for hydrocarbon reduction is not further discussed in this chapter.

5. Oxides of Sulfur

At present, there is no NSPS for SO_x emissions from FCC regenerators. The sulfur content of the feed to FCC's has been increasing. It is estimated that the SO_x concentration in the flue gas will increase from 885 ppm

mated that the SO_x concentration in the flue gas will increase from 885 ppm in 1978 to 905 ppm^x in 1988 (national averages, see Chapter V). The control technology for SO_x reduction is reliable and includes various processes to suit the individual^x situation. The processes suited for application to FCC regenerators are described in detail in the latter part of this chapter.

6. Other Pollutants

Other pollutants from FCC regenerators include HCN and NH_3 . The concentration of both of these pollutants is 200 ppm each in flue gas from traditional regenerators and 10 ppm each in flue gas after CO boilers. These chemicals are destructed at high temperature. The control technology for reduction of these pollutants is the same as the control technology for reduction of hydrocarbons. Therefore, the same logic for application of NSPS applies.

It should be mentioned that the reduction of HCN and NH_3 in HTR or CO boilers will increase the concentration of NO_x emissions.³ For example, the NO_x emissions in flue gas from conventional^x regenerators is <10 ppm; however^x, the NO_x emissions in flue gas after CO boilers is 100-200 ppm. (Some NO_x in CO^x boilers forms from nitrogen in the air supply and nitrogen in the oil^x feed to the CO boiler.)

B. SO_x EMISSION CONTROL

Reduction of SO_x emissions can be accomplished by a variety of methods including:

- Use of low-sulfur fuel as FCC feedstock,
- Removal of sulfur from the FCC feedstock, and
- Removal of SO_x from FCC regenerator flue gas.

Removal of sulfur from the FCC feedstock can be accomplished by direct hydrodesulfurization since FCC feed is low in asphaltene materials. Switching to low-sulfur feeds is the easiest option to implement and requires minimal capital investment. However, it is not a universal solution because there is not enough low-sulfur crude available to satisfy the potential demand. Hence, in most cases, desulfurization of FCC feedstock or desulfurization of regenerator flue gas must be employed to satisfy the sulfur emission requirements.

Various sulfur removal processes have been, or are being, developed in each of the sulfur removal methods mentioned above. In the remainder of this chapter, we discuss both SO_x removal methods as they have potential application in the refinery industry.

C. FLUE GAS DESULFURIZATION PROCESSES

Flue gas desulfurization (FGD) is the removal of sulfur compounds after combustion of the fuel. Fuel combustion is associated with FCC operation, since the coke deposited on the catalyst is removed by combustion with air. Sulfur present in the coke appears in the flue gas in the form of SO_2 and SO_3 . The flue gas from the FCC regenerator may contain SO_3 up to 50% of the total SO_x ; ¹⁰ although the actual SO_2/SO_3 ratio is uncertain. The high concentration of SO_3 (compared to other combustion processes) may be due to the presence of metallic compounds such as vanadium which may act as a catalyst in the formation of SO_3 .

The advantages of FGD systems (compared to desulfurization of FCC feed) are flexibility of feed supply and lower energy consumption.

Flue gas desulfurization processes may be classified according to the final form of the sulfur removed from the flue gas as follows:

- Elemental sulfur
- Direct sulfuric acid
- Waste salts, and
- Concentrated SO_2 .

Only three processes, Exxon's jet ejector scrubber (a waste salt process), the Wellman-Lord process (concentrated SO_2 process), and the UOP process (concentrated SO_2 process), have actually been applied to refineries (the Claus plant or boilers) and only the Exxon scrubber has been used with a fluid catalytic cracker. Because of this, we have concentrated the evaluation in this report on these three processes applicable to the refinery industry; however, other processes are mentioned briefly.

1. Elemental Sulfur Processes

These processes produce elemental sulfur or hydrogen sulfide directly, with no intermediate production of concentrated SO_2 . Hydrogen sulfide can be converted directly to elemental sulfur using commercially available technology (the Claus process). EPA is currently reviewing proposals based upon some of these processes for funding of a 100-megawatt coal-fired demonstration plant for a sulfur recovery process. Processes in this category include:

- Charcoal absorption - Westvaco, Foster-Wheeler
- Citrate process - Arthur G. McKee
- Potassium Thio sulfate system - Conoco Coal Development

- Sodium phosphate process - Stauffer Chemical/Chemico
- Dry carbonate process - Atomics International
- Ammonia process - Catalytic

These processes are in the earlier stages of development, and cannot be expected to have any important commercial impact until about the mid-1980's.

2. Direct Acid Processes

In these processes, sulfuric acid is produced directly with no intermediate concentrated SO_2 gas stream. A more dilute acid is produced than the normal commercial 98% acid grade. Operations involving this approach have been unsuccessful to date and the outlook is not promising.

3. Waste Salt Processes

a. General

These processes produce varying types of sulfide and sulfate salts which must be disposed of in an environmentally acceptable manner. They account for over 90% of the systems currently committed for SO_x removal and can be expected to sustain this strong position in applications which will become operational over the next ten years. Of these waste salt or "throw-away" processes, a very large fraction involve some version of lime or limestone slurry scrubbing to produce a solid waste calcium sulfite/sulfate for disposal. Most of these systems are applied to large units where the gas flow rates are 300,000 scfm and higher. The processes based on lime/limestone suffer from problems of scaling of the scrubber due to the presence of the insoluble salts in the scrubber liquor. Consequently, process availability has been low. Also, disposal of sludge from FGD processes in refineries may be a problem.

Soluble salts, such as sodium salts, may be used to avoid the scaling problems in the scrubber; however, sodium salts are expensive. In some processes sodium salts are regenerated using lime or limestone, which results in the formation of waste cake. If the sodium solution is not regenerated (once-through), it is necessary to reduce the COD of the wastewater before discharging the scrubber bleed. In some cases it may also be necessary to reduce the insoluble and soluble salts.

In the once-through sodium system the spent liquor from the scrubber is not regenerated. If the particulates and SO_x are removed simultaneously in the scrubber, the problems present in the regeneration of the scrubber solution are increased. In a once-through sodium system, particulates and SO_x can be removed simultaneously without these major problems.

Various types of contacting devices can be used to remove particulates and SO_x . These devices include venturi, jet ejector, tray tower, packed

tower, TCA scrubber, spray scrubber, etc. The particulate collection efficiency of the spray scrubber is very low. Collection devices such as tray scrubbers, packed scrubbers, and TCA scrubbers are likely to plug up if particulate matter is present. The remaining devices such as conventional venturi scrubbers and jet ejector venturi scrubbers can be used to remove particulates and SO_x simultaneously.

b. Exxon Jet Ejector Liquid Scrubber Process Description

The application of jet ejector liquid scrubber to FCC units for simultaneous removal of SO_x and particulates, marketed by Exxon, is shown in Figure III-1. The schematic of the FCC jet ejector scrubbing system is shown in Figure III-2.

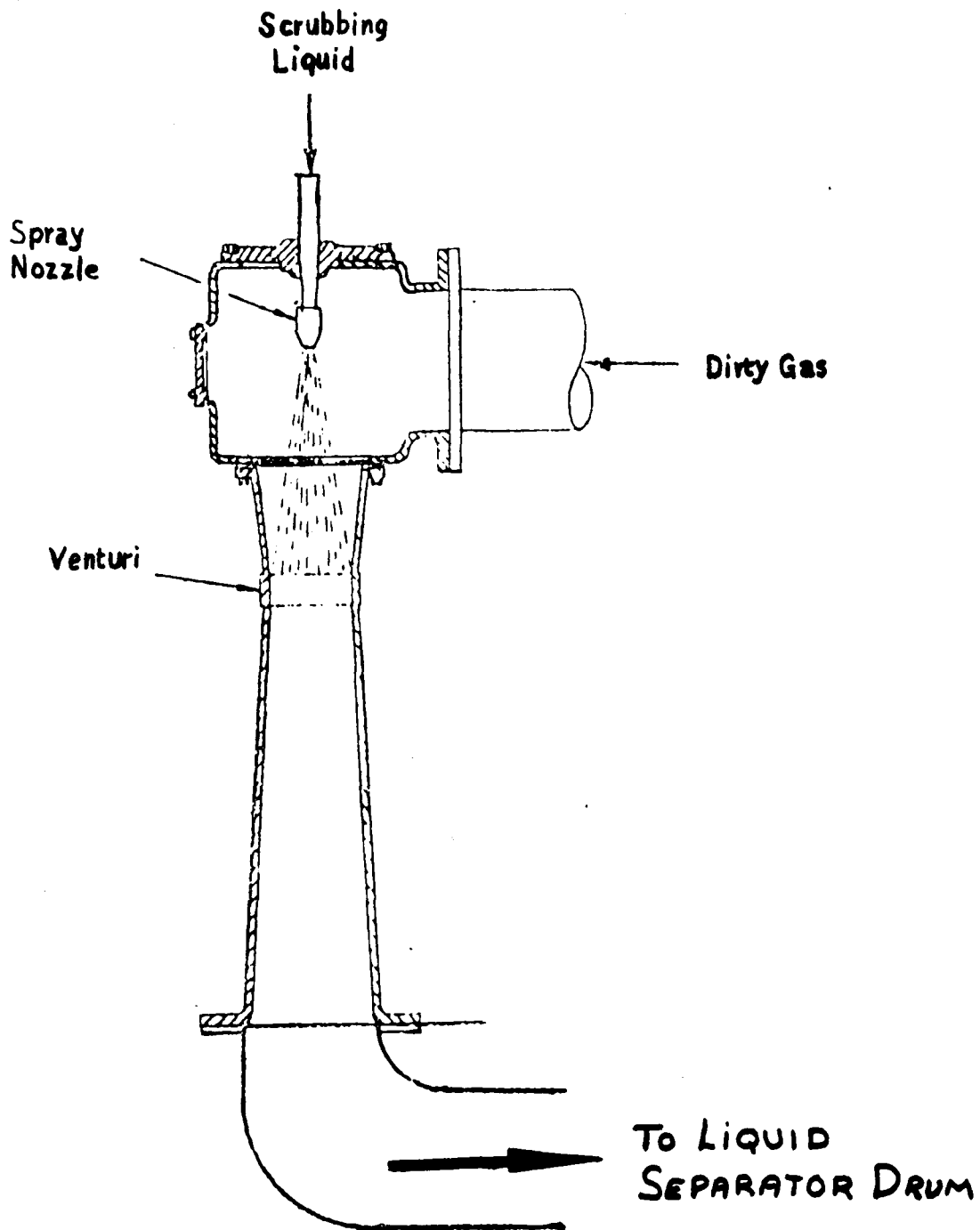
The scrubber liquid passes through a spray nozzle which breaks the liquid stream into droplets. These droplets have size and velocity characteristics suitable for contacting with the flue gas to provide the scrubber efficiency.

The dust-laden flue gas is drawn into the body of the scrubber by the draft-inducing action of the liquid spray. The gas is intermixed with the scrubbing liquid and both enter the venturi section of the scrubber. In the venturi section, the liquid and gas enter an area of intense turbulence. Here, the liquid droplets strike and capture the particles in the gas stream and the SO_x in the flue gas is absorbed in the liquid. Also, within this venturi section momentum transfer to the gas occurs creating a pressure build-up across the unit which will move the flue gas through the system from the inlet of the scrubber to the outlet.

After passing through the venturi section, the mixture of gas and droplets is sent to a separator where the clean gas is separated from the contacted water and discharged to the atmosphere, after reheating.

A conventional venturi scrubber operates in much the same way as the jet ejector scrubber; except that momentum transfer takes place from the gas phase to the liquid phase. The liquid is broken up into small droplets due to the high gas velocity in the venturi scrubber. Power plants and steam plants have long used wet gas scrubbing of flue gases to remove SO_x and particulates using conventional venturi scrubbers with associated stack fans to achieve pressure balance. The difference between the two is that in the conventional venturi scrubber the energy is provided by a fan on the gas side, whereas in the jet ejector scrubber energy is provided by a pump on the liquid side. In the conventional venturi scrubber, it is also necessary to have a liquid pump to provide the flow of liquid to the venturi.

In the scrubber, absorption of SO_2 takes place with the following chemical reactions:



Source: Exxon R&E.

Figure III-1 Jet Ejector Venturi Scrubber

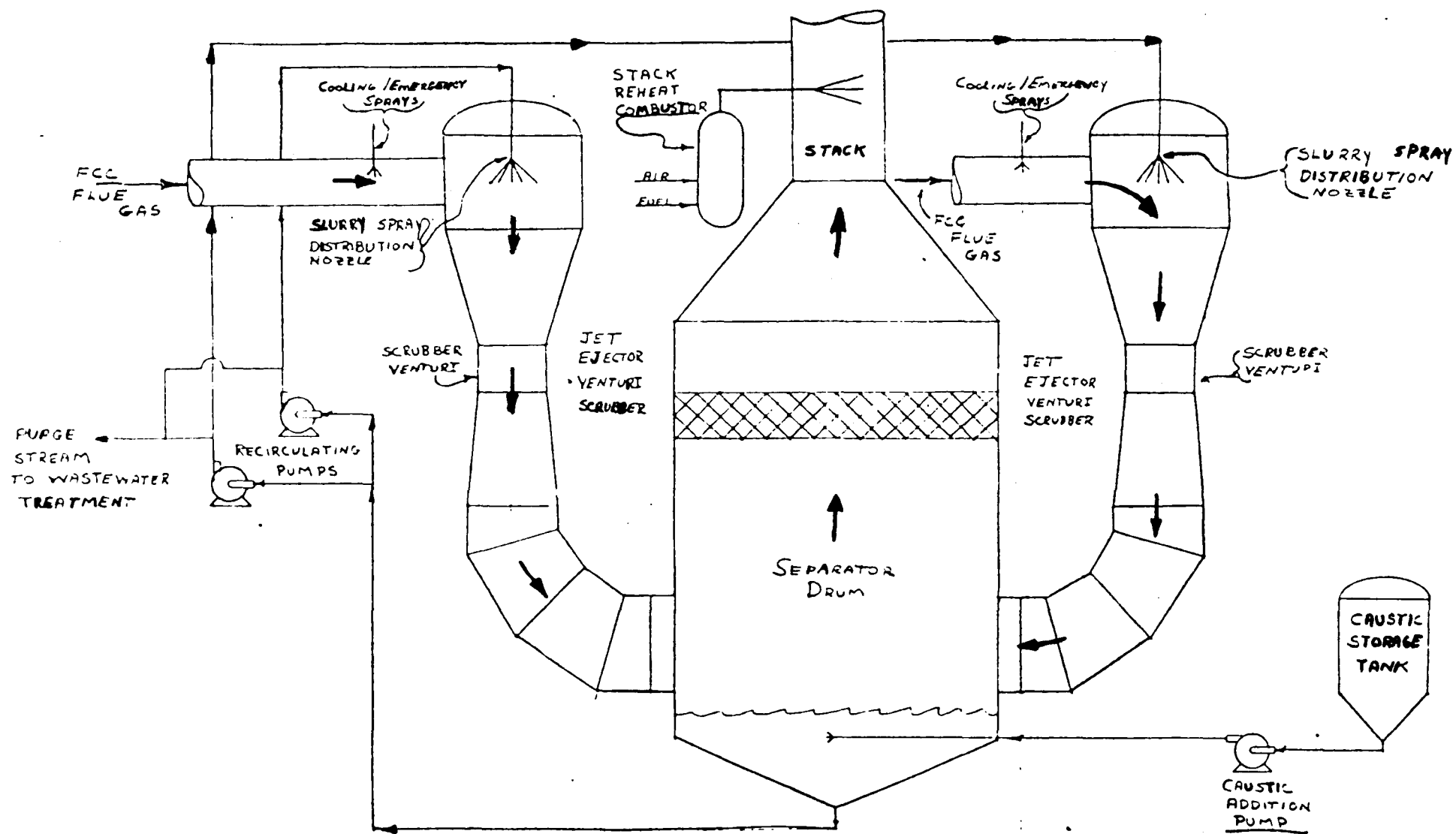
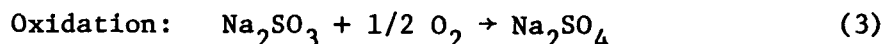
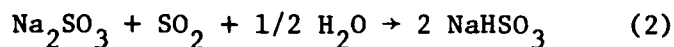
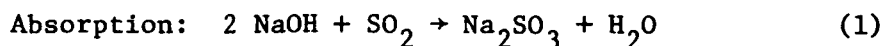


Figure III-2 Schematic of Exxon FCC Jet Ejector Scrubbing System



The purge stream from the scrubber will contain soluble salts of sulfites and sulfates. The concentration of the soluble salts is generally below 5%. If the particulate collection and the SO_x absorption are carried out simultaneously in the wet scrubber, the scrubber bleed will contain insoluble salts in addition to soluble salts. It will be necessary to treat the scrubber bleed before it can be discharged. The water treatment should include removal of insoluble salts, reduction of COD, and in some cases reduction of soluble salts.

Technical Considerations

The venturi scrubbers are in general very flexible and changes in the gas flow rate, temperature of the gases, and the humidity of the gas have very little effect on the collection efficiency. Furthermore, the outlet concentration of the SO_x in the flue gas can be easily controlled by adjusting the pH of the scrubber solution.

The collection efficiency of the scrubber can be changed by changing the input energy to the scrubber. This can be done by increasing the pressure drop in the venturi for conventional venturi scrubbers and increasing the pressure of the motivating fluid in the jet ejector scrubber. Thus, the collection efficiency of the scrubber can be changed to meet the future considerations.

As discussed earlier, the scrubber may not be able to reduce the outlet SO_x concentration to the same level when the inlet SO_x concentration is high. This is because the jet ejector scrubber represents a single stage co-current operation. If more stages are required, provision should be made for additional contact stages downstream of the ejector in the form of a tray or a packed scrubber. The gases coming into the tray or packed scrubber will be particulate-free and, therefore, the problem of scrubber plugging will not be present.

The gases coming to the scrubber are cooled with spray water in order to decrease the flue gas temperature. The SO_3 in the flue gas will condense and form mist at this temperature. It will be difficult to capture these submicronic mist particles since they will generally escape through the venturi scrubber. The SO_3 concentration in the Exxon FCC units has been found to be 1-3% of SO_2 ; thus, the problem of SO_3 mist has not been experienced in the Exxon facilities.

In a once-through sodium system, the scrubbing solution is not regenerated. Particulate and SO_x removal can therefore be conveniently carried out in the same equipment which will reduce the system's initial capital cost.

If particulate removal is carried out in the scrubber, the liquid bleed from the scrubber will contain insoluble solids. It is expected that the handling of this slurry will increase erosion and solids deposition problems. The liquid handling system should therefore have erosion-resistant materials where slurry is contacted.

The scrubber bleed will contain both soluble and insoluble solids, making it necessary to treat the wastewater before it can be discharged. The insoluble solids may be removed in the thickener/clarifier. Treatment of the clarified wastewater may be combined with treatment of other refinery waste streams, which will lower the operating cost of pollution control for FCC units.

The caustic used in a once-through sodium scrubbing system represents a significant operating cost. The caustic consumption is directly proportional to the inlet SO_x concentration. Thus, if the inlet SO_x concentration is increased from 500 ppm to 3,000 ppm, the caustic consumption will increase sixfold. The economics of the system will therefore vary depending on the inlet SO_x concentration.

Pollutant Removal Efficiency

The pilot plant performance of the Exxon jet ejector scrubber is shown in Table III-1. The SO_x removal efficiency was 95-99% with SO_x inlet concentrations of 200-500 ppm. Although the SO_x concentration in the inlet to the scrubber may be as high as 3,000 ppm for potential applications, no data are available on the operation of the jet ejector scrubber for inlet SO_x concentrations higher than 500 ppm.

The catalyst particulate concentration in the pilot plant inlet gas was 0.1-0.3 gr/scf. Under these conditions the collection efficiency was 85-95%. In general, the particulate concentrations to the scrubber may vary from .02-1.5 gr/scf. If the particle size distribution remains the same, the collection efficiency will remain constant. Thus, the outlet grain loading will increase in direct proportion to the inlet grain loading.

The NO_x removal efficiency of this scrubber is expected to be low.

Status of Process

The applications of Exxon jet ejector scrubber to FCC units are shown in Table III-2. Overall performance has been good. There have been small metal loss problems in the scrubbing liquid delivery system due to erosion and corrosion, but solutions to these problems are being implemented. The service factors on the two Baytown scrubbers have been 94% and 93%, respectively, since the beginning of 1975. This service factor is lower than for FCC in general, therefore, occasional by-passing of the scrubber would be necessary to avoid outage of the FCC. The SO_x removal efficiency and the particulate removal efficiency have been >90%.

TABLE III-1

PILOT PLANT PERFORMANCE DATA
FOR EXXON ONCE-THROUGH SODIUM SYSTEM

<u>Range of Pollutant</u> <u>Loadings to Scrubber</u>	<u>Collection Efficiency</u> <u>Percent</u>
<u>SO_x</u>	
200-500 ppm	95-99
<u>Particulate</u>	
0.1-0.3 gr/SCF	85-95
<u>Condensables</u>	
0.1-0.2 gr/SCF	<90

Source: Exxon Research and Engineering

TABLE III-2

STATUS OF EXXON JET EJECTOR VENTURI SCRUBBER APPLICATIONS
TO THE FCC SYSTEMS

<u>Location</u>	<u>Design Size ACFM</u>	<u>Startup Date</u>
Baytown, Texas	300,000	March 1974
Baytown, Texas	510,000	May 1975
Baton Rouge, Louisiana	860,000	February 1976
Bayway, New Jersey	590,000	May 1976

Source: Exxon Research and Engineering

4. Concentrated SO₂ Processes

These processes produce concentrated SO₂ gas streams from dilute flue gas SO₂. Conventional, commercially proven technology is available for conversion of concentrated SO₂ produced in these processes to either liquid SO₂, sulfuric acid, or elemental sulfur. Liquid SO₂ is produced by compression of the SO₂ stream after the gas from the process has been concentrated and dried.

The conventional technology involving reaction of H₂S and SO₂ to produce sulfur (Claus process) can be used. H₂S is normally generated in the refineries. Thus, the processes generating SO₂ are attractive for application to FCC regenerators.

The processes generating SO₂ may be either wet or dry. The leading wet process is the Wellman-Lord process and the leading dry process is the Shell/UOP process. These are described in the following sections.

a. Wellman-Lord Process²⁶

Process Description

The Wellman-Lord process was developed by Davy Powergas, Inc., formerly Wellman-Power Gas, Inc., of Lakeland, Florida.

The flow scheme for the basic process is shown in Figure III-3. The SO₂-rich gas is contacted countercurrently in the absorber by the sodium sulfite solution and exits the absorber top stripped of SO₂. The solution leaving the bottom of the absorber, now rich in bisulfite, is discharged to a surge tank and then pumped to a proprietary evaporator/crystallizer in the regeneration section.

Low pressure steam is used to heat the evaporator and drive off SO₂ and water vapor. The sodium sulfite precipitates as it forms and builds a dense slurry of crystals.

The gas stream leaving the evaporator is subjected to partial condensation to remove the majority of the water vapor before the product SO₂ is discharged from the process. The condensate in the mixture with the sulfite slurry stream withdrawn from the evaporator is used for re-dissolving the slurry in the dissolving tank. The sulfite lean solution is then pumped to a surge tank and fed back to the absorber.

Gas precleaning is recommended in the Wellman-Lord system. If the gases are cooled in the precleaning device, however, the SO₃ will be present as fine mist particles. Collection of these submicron particles is difficult in a low energy scrubber, therefore, most of the particles will escape the scrubber.

The process is based on a sodium sulfite/bisulfite cycle. In addition, sodium sulfate (Na₂SO₄), which is nonregenerable in the normal process, is

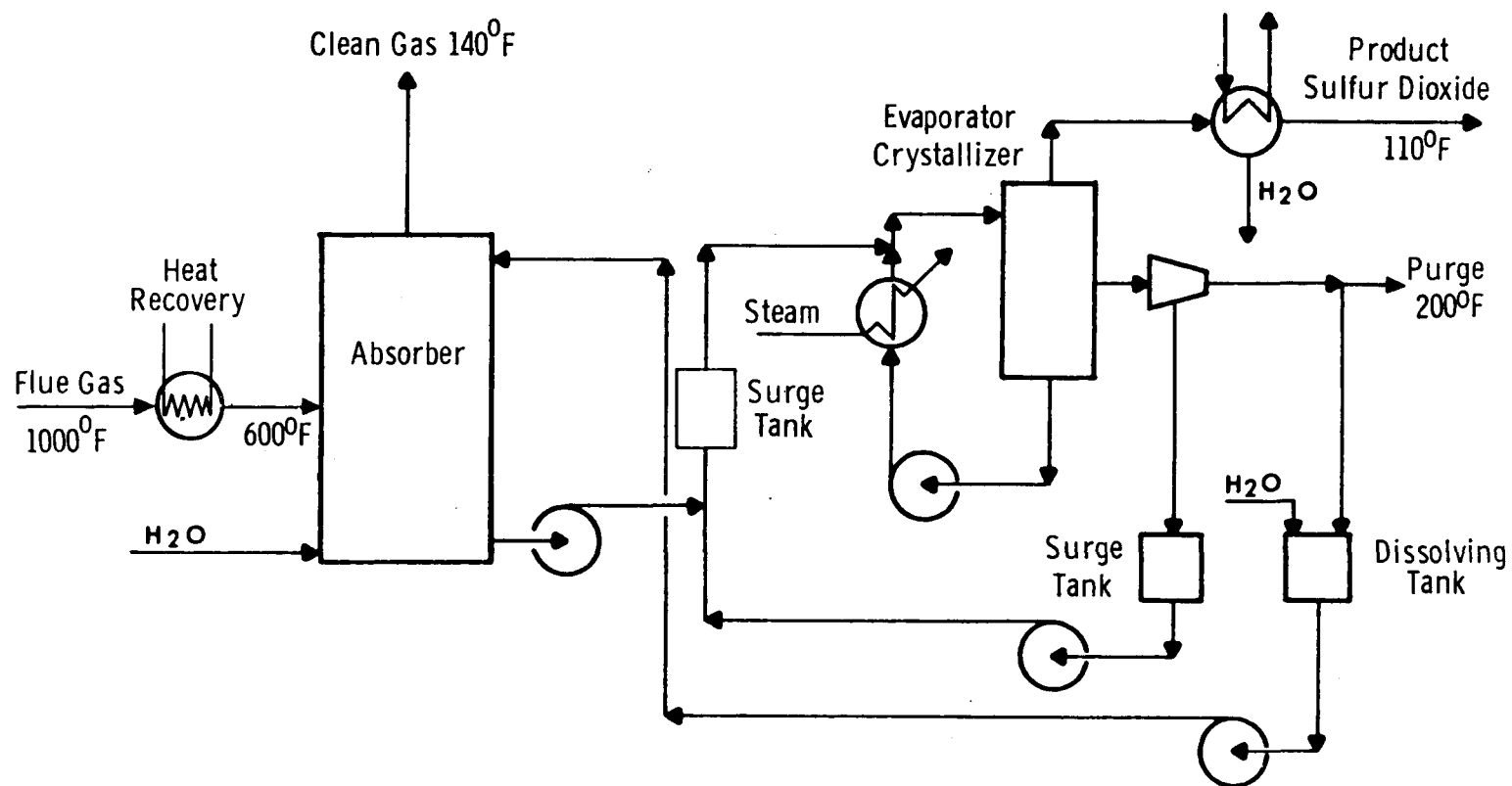


Figure III-3 Wellman-Lord, Inc., Sulfur Dioxide Recovery, Sodium System

formed in the absorber as a result of oxidation of sodium sulfite and collection of sulfur trioxide.

The sodium sulfate is controlled at a level of approximately 5 wt. % in the absorber feed stream by use of a continuous purge from the system. High concentration of SO_3 in the flue gas, if not removed in the gas pretreatment, would result in an increased concentration of Na_2SO_4 and proportionally increased purge of the scrubbing liquor.

A makeup of caustic is required to replace that lost in the purge stream. The caustic makeup solution reacts with the sodium bisulfite in the absorber solution to form additional sodium sulfite. Soda ash (Na_2CO_3) can also be used as the makeup source of sodium.

The simple regeneration scheme of the patented Wellman-Lord process relies on the favorable solubilities of the sodium system. The bisulfite form has almost twice the solubility of sulfite at the temperatures considered for the process. Because of this it is possible to feed the absorber with a saturated sulfite solution, or even a slurry, without any fear of additional crystallization or scale forming despite considerable evaporation of water. This is because as SO_2 absorption proceeds, the composition of the solution is shifted in the direction of increasing solubility.

Technical Consideration

The major concern with the Wellman-Lord system in this application is sulfate formation. The system may be unsuitable for application to the FCC regenerator due to possible high sulfur trioxide levels in the gas leaving the catalyst regenerator. The SO_3/SO_2 ratio in the catalyst regenerator depends on process conditions and the presence of metallic compounds such as vanadium which may act as oxidizing agents. Therefore, the ratio of SO_3/SO_2 in the flue gas will vary with changes in the process conditions and changes in the oil feed. The presence of SO_3 in high concentrations will result in excessive sulfate formation.

The Wellman-Lord process must avoid a buildup of contaminants in the system liquor. Possible contaminant sources include not only all by-product formation in the system (Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, S, etc.) but also all soluble and insoluble contaminants picked up from the flue gas and process makeup water. However, the most significant of these is sulfate. Since it cannot be thermally regenerated sulfate must be purged from the system in some type of bleed stream. This purge also removes other contaminants from the system; however, the purge rate will normally be determined by the amount of sulfate formed. The effect of this purge requirement will be directly translated into process economics--in the capital investment for the purge treatment facility and the operating costs associated with the makeup sodium and purge disposal. Because these costs can be substantial and because process acceptability may be evaluated in terms of lost sodium value and waste disposability, a considerable process development effort has been expended in determining the various factors governing the

rates of sulfate formation and developing methods for minimizing both sulfate formation and the attendant sodium losses in the required purge.

The majority of the sulfate is formed in the absorption system both from sulfite oxidation and from absorption of sulfur trioxide. To some degree the high solution concentrations used in the Wellman-Lord system tend to reduce the sulfite oxidation because oxygen solubility is greatly reduced at high solution concentrations. However, this is not effective against high SO_3 levels. Work is being directed toward further reducing oxidation by introducing anti-oxidants into the system. The concentration of SO_3 present in the regenerator flue gas must be established before the feasibility of using this process can be decided.

The Wellman-Lord system is flexible in that it can handle wide variations in gas flow rate, temperature, humidity, and SO_2 concentration. The exit SO_2 concentrations can be controlled by adjusting the pH of the absorbing solution.

The regeneration section and absorber are separated by surge tanks, therefore, the regeneration section may be located away from the absorber section. If more than one absorber is used in the refinery, a common regeneration system may be used. These advantages may help reduce space problems.

The solution concentrations in the Wellman-Lord system are close to saturation, thus, the flow rates in the system are small. However, the possibility of precipitation of salts is increased.

The Wellman-Lord system generates SO_2 -rich gas. This can be further processed in a Claus-type facility at the refinery.

Pollution Problems

The sulfate crystallizer in the Wellman-Lord system generates waste solids. If no impurities are present, it will contain 85% Na_2SO_4 , 15% Na_2SO_3 crystals, and some process solution trapped in between the crystals. It will be necessary to dispose of these solids.

The quantity of solids generated will depend on the amount of oxidation of sodium sulfite to sodium sulfate and the absorption of SO_3 from the flue gas. Presence in the flue gas of 1-2% SO_3 (percent of total SO_x present in the flue gas) and 2% O_2 may result in 5-6% oxidation of the sulfide solution. This will generate dry waste solids representing 6-7% of the SO_x absorbed. The total waste solids will be dry solids plus the liquor containing dissolved solids.

System Collection Efficiency

The outlet SO_2 concentration with the Wellman-Lord system may be as low as in the once-through sodium system. Concentrations in the range of 50 ppm are possible.

The Wellman-Lord system has a tendency to accumulate impurities which must be purged from the system. Therefore, the particulate collection must be carried out upstream of the scrubber.

The system has poor collection efficiency for NO_x . Efficiencies for hydrocarbon and CO removal are negligible.

System Reliability

The Wellman-Lord system is a fully-developed SO_2 control system. It has been commercially applied to nearly 25 flue gas sources, sulfuric acid plants, Claus plants, and utility boilers. The system availability is more than 95%. It has not been applied to FCC units.

b. Shell Flue Gas Desulfurization Process (UOP)

This process was developed by Shell International Research, The Netherlands, and is presently licensed by Universal Oil Products, Des Plaines, Illinois.

Process Description²⁶

The Shell Flue Gas Desulfurization (SFGD) process uses a dry acceptor in a static packed bed to remove SO_2 from gaseous streams. The CuO acceptor contained in two or more identical reactors, is subjected to successive stages of acceptance and regeneration at approximately the same temperature. The net effect is that SO_2 , free of oxygen and particulates, is obtained concomitant with the required degree of gas desulfurization.

Figure III-4 is a simplified illustration of the SFGD process equipment arrangement. The SO_2 -rich gas passes through the acceptance reactor(s) for about 45-60 minutes, until the cumulative slip (break-through) of SO_2 into the treated gas has reached a designated SO_2 concentration. The SO_2 -rich gas stream is then switched to a reactor containing regenerated acceptor, and the loaded acceptor is regenerated. Gas from the purging of the reactors between acceptance and regeneration is treated in the accepting reactor.

CuO is outstanding as an acceptor in this application in that it readily forms sulfate with SO_2 in the presence of oxygen at, ideally, about 700-750°F, and can be satisfactorily regenerated with reducing gas to yield concentrated SO_2 at about the same temperature.

Technical Considerations

In general, adsorption systems have plugging problems; therefore, the incoming flue gas must be free of particulate matter. However, in the Shell/UOP system the flue gas passes along the surface of the acceptor packages and not through the acceptor material. This prevents pressure-drop buildup due to the deposition of particulate material present in

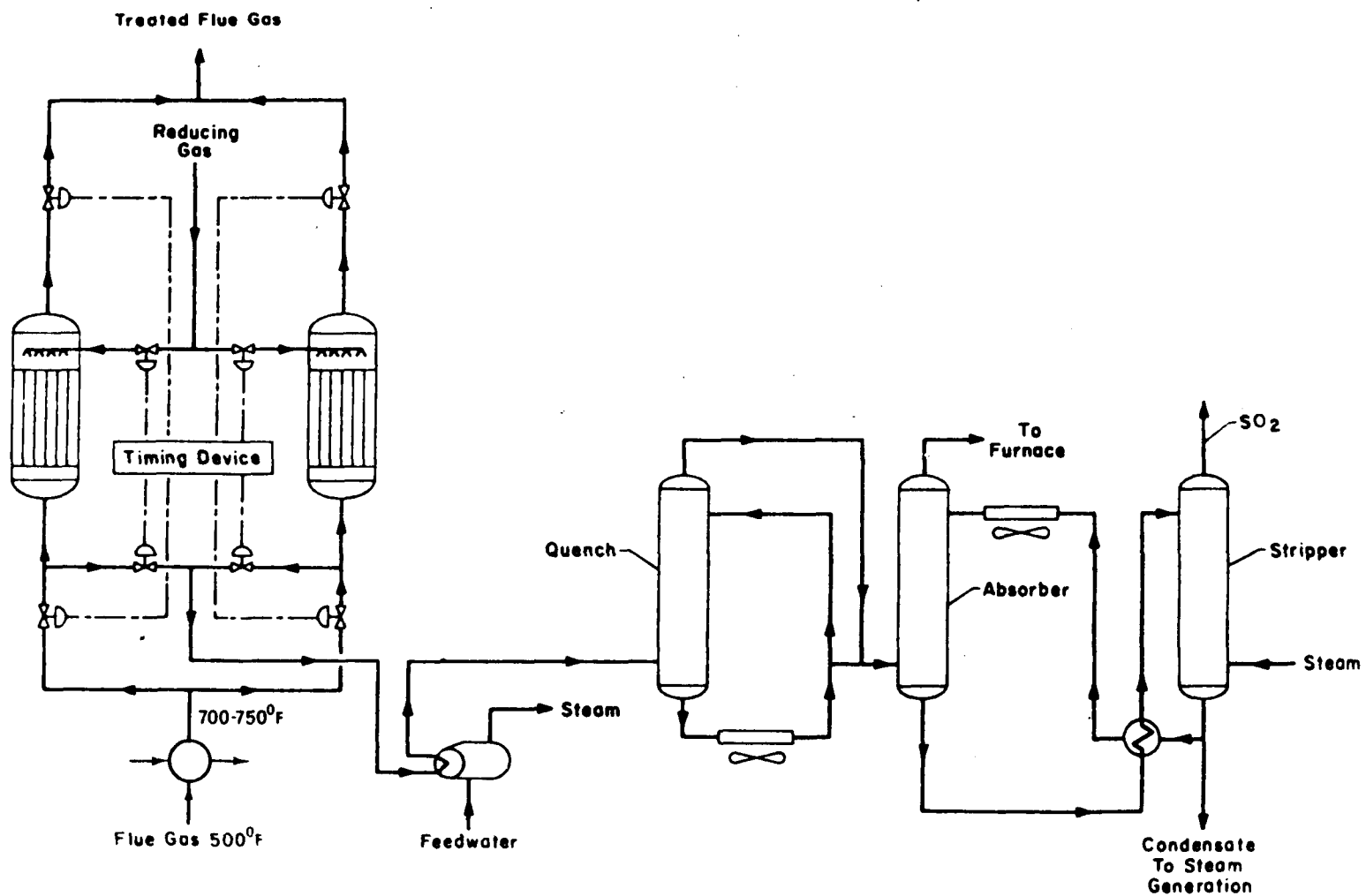


Figure III-4 Shell Flue Gas Desulfurization Unit

the flue gas. The system has been shown to operate on flue gas containing particulate loading of 0.1 gr/scf with no evidence of plugging or fouling.

In some FGD processes, oxidation or the presence of SO_3 creates problems during regeneration. In the Shell/UOP process, however, the SO_3 does adsorb; thus, the presence of SO_3 will not be a problem in this process.

The particulate collection efficiency of the UOP adsorption system is poor by design and the appropriate process location is downstream of the ESP. If sulfur trioxide were present in mist form, it would escape through the adsorption reactor. Since the adsorption is carried out at high temperature (700-750°F), the SO_3 will be present in the gas form and will be adsorbed on the acceptor.

Oxygen in the flue gas is used in the adsorption reaction and in the reactions during regeneration. The Shell/UOP process has been tested on boiler flue gas which normally contains an oxygen concentration equal to 4-6 percent. SO_x concentrations in the flue gas from a boiler are in the same range as concentrations in the flue gas from a FCC regenerator. The oxygen concentration in flue gas from the FCC regenerator system is 0.5 to 2 percent. The effect of this lower oxygen concentration on the SO_x removal efficiency is not known. The ratio of oxygen concentration to SO_x concentration in the FCC regenerator flue gas is 2 or higher (minimum oxygen concentration of 0.5 percent oxygen and maximum SO_x concentration of 2,500 ppm). The theoretical oxygen to SO_x mol ratio is equal to 1. Therefore, the effect of decreased oxygen concentration may not be significant.

Most of the FGD processes producing concentrated SO_2 , concentrated H_2SO_4 , or elemental sulfur use reducing gas (natural gas, H_2 , CO, etc.). Reducing gases are generally in short supply and therefore the applicability of these concentrated sulfur processes to FGD is limited. In petroleum refineries, however, reducing gas (H_2) is generally available and therefore supply of hydrogen should not be a problem.

As indicated in the process flow schematic, the reactor beds are automatically cycled from acceptor mode to regeneration mode by the use of sequential timers and motor-activated butterfly valves. To prevent leakage of reducing gas into the on-line reactor, special, large, tight shut-off flue gas valves are required. In addition, pressure surges caused by reactor switching can influence operation of the upstream process and are therefore undesirable. The effect of these surges is minimized by the use of an "open bypass" which continuously recycles a small quantity of treated flue gas. The performance at existing facilities has confirmed the operability of the sequential switching and bypass system.²²

The inlet temperature to the fixed bed reactor must be 700-750°F. The flue gas temperature downstream of the particulate control device (ESP) is normally in the range of 300-450°F. Therefore, to obtain higher flue gas temperature, less heat may be recovered in the CO boiler. This

also requires a hot precipitator instead of a cold precipitator. On the other hand, the higher flue gas temperature may be obtained by using a preheater. The heat requirement in a preheater may be minimized by using a heat exchanger to recover heat from the clean gas. The preheater application may be more suited for a new situation than for existing facilities due to the arrangement of in-place equipment and space limitations.

The flue gas from a wet system is saturated at the downstream of the scrubber. Therefore, it shows plume and sometimes results in acid rain near the stack. It is necessary to reheat the gases to avoid this problem. The problem of visible plume and acid rain is not present in the dry systems.

Other Pollution Considerations

The product from the Shell/UOP process is concentrated SO₂ gas. The gas can be sent to a Claus-type unit to generate sulfur. Since the Shell/UOP process is a dry system and therefore no liquid effluents are generated in the process, it will be necessary to replace catalyst after 1-2 years of operation. This will create solid waste. The quantity of solid waste is very small.

Final Concentration

The operation of the Shell/UOP system has demonstrated 90 percent SO₂ removal efficiency when applied to boiler stacks. It is expected that proper operation of the system on FCC regenerator flue gas will have the same efficiency. By design, the system has poor collection efficiency for particulate removal. The SFGD system is capable of NO_x removal by addition of a suitable adsorbent according to UOP. Performance data are not known.

Status of Process

The feasibility of the process was tested in a demonstration unit erected in 1967 in the Shell refinery at Pernis, The Netherlands. The Pernis unit handled 600 scfm of flue gas containing 0.1 to 0.3 volume percent SO₂. A total of 20,000 hours of testing was accomplished to establish the stable activity of an acceptor based on a reinforced alumina support. The estimated acceptor life is in excess of 8,000 cycles or 1-1/2 years.

A commercial unit was started in August 1973 in Yokkaichi, Japan to treat 80,000 scfm of oil-fired boiler flue gas containing a maximum of 2,500 ppm SO₂ at the Showa Yokkaichi Sekiyu refinery. The SO₂ removal efficiency is 90 percent and the hydrogen consumption is about 0.2 lb H₂/lb sulfur removed. The SO₂ produced in regeneration is totally transferred to the Claus unit by the absorption/stripping section.

The first installation of the SFGD process on a coal-fired boiler in the United States is a 0.6 Mw pilot plant at Tampa Electric Company's

Big Bend Station which went on-stream in June 1974. Bottled hydrogen is used for regeneration and the SO_2 is returned to the stack. The pilot plant slip stream has been taken before and after the flue gas leaves a cold electrostatic precipitator so that the CuO reactor has experienced the full grain loading from the boiler. The particulate entering the reactor passes on through and there has been no evidence of plugging or fouling. The SO_2 removal efficiency ranges from 75 to greater than 90 percent depending upon process parameters.

The system has not been applied to desulfurize flue gas from FCC regenerators.

D. DESULFURIZATION OF FCC FEED

The feed to the FCC may be desulfurized as an alternate to flue gas desulfurization to meet SO_x emission standards for FCC regenerators. Desulfurization technology^x is very well known to petroleum refiners and can be applied to almost any petroleum stock except certain heavy resids. Typically, FCC feedstock (mainly vacuum gas oil) contains 0.51 to .36 weight percent of sulfur.²³ However, vacuum gas oil obtained from Louisiana, Nigeria Forcados, Oklahoma, Algerian-Hassi Messaoud, and Indonesia, Minas charge stocks contain less than 0.5 percent sulfur.

A portion of the sulfur in the FCC feedstock is deposited with the coke on the catalyst. The sulfur in the coke leaves as SO_x during regeneration of the catalyst. The sulfur concentration of the coke is 0.7-3 times the sulfur concentration in the FCC feed. The sulfur in the coke represents 2-30 percent of the total sulfur in the feed.²⁰

The range of sulfur concentration in coke and sulfur concentration as a percentage of feed sulfur is large because the relationship is very complex. The thiophenic sulfur compounds in the feed have a tendency to remain on catalyst with the coke. The sulfur concentrations in the coke as a percentage of feed to the FCC is high for feeds containing thiophenic sulfur compounds. Since hydrotreating removes essentially all the non-thiophene sulfur compounds, the sulfur distribution for hydrotreated feedstocks is significantly different than for virgin feedstocks.

Figure III-5 relates SO_x concentration in the flue gas and coke sulfur content. R is the ratio of CO_2/CO in the flue gas. If the concentration of CO in the flue gas is reduced to meet NSPS standards, the value of R approaches ∞ . The concentration of CO in the flue gas may be reduced by high temperature regeneration or using a CO boiler. To achieve a 300-600 ppm SO_x level, the coke sulfur content must be 0.36-0.72%. Since the ratio of coke sulfur content to feed sulfur content is 2-3, the feed sulfur must be reduced to 0.12-0.36% by hydrotreating.

The technology for vacuum gas oil desulfurization is well-established. Up to 97% of the feed sulfur can be removed, but typically, 90% removal

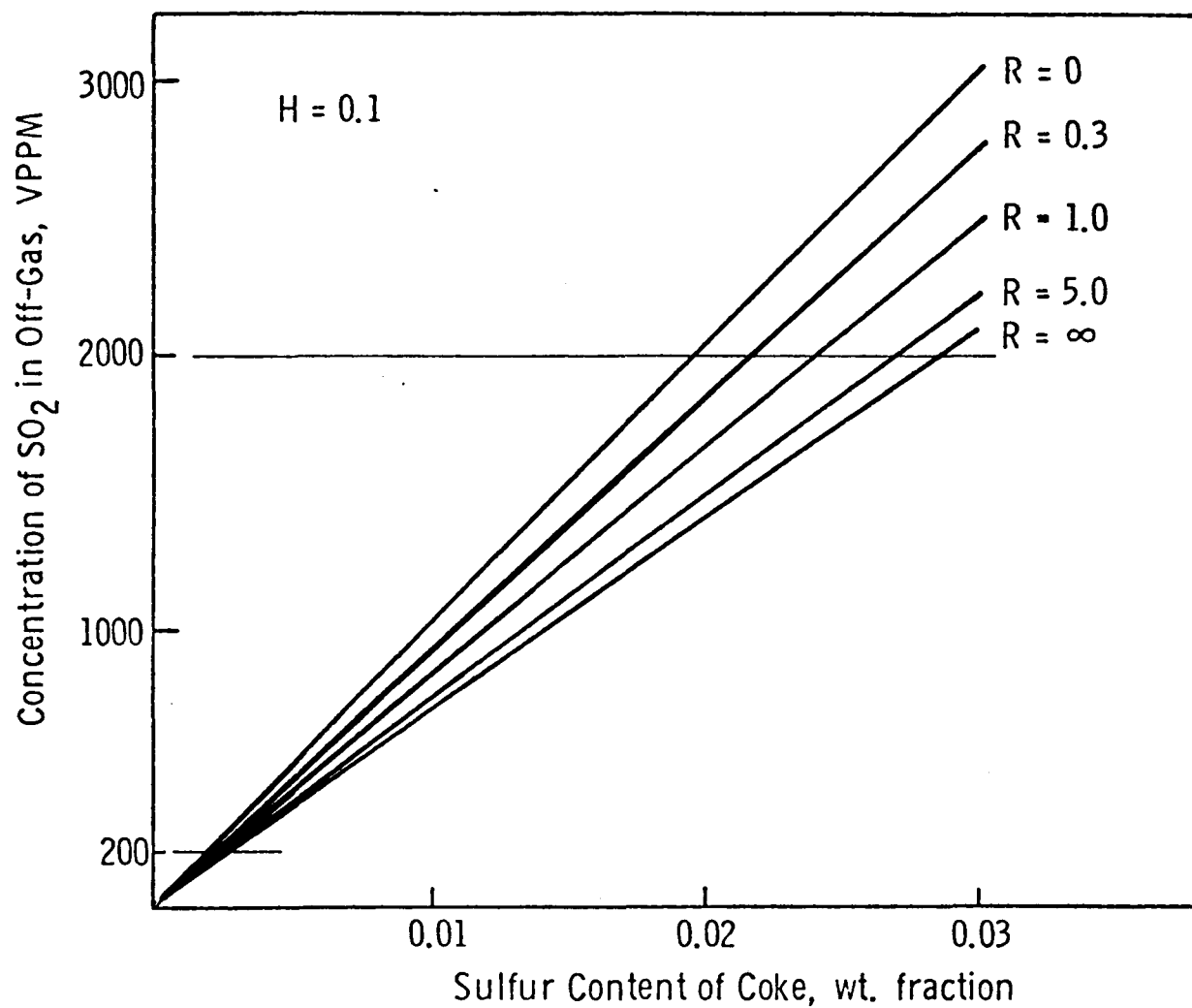


Figure III-5 SO_2 Concentration in FCC Regenerator Off-Gas

is used as an economic guideline. Thus, FCC feed desulfurization is a possible control option to meet SO_x emission standards.

There are several processes available for feed hydrodesulfurization. These processes are shown in Table III-3. All these processes are reliable in operation and familiar to the refinery industry.

Process Description

The FCC feedstock is mixed with hydrogen-rich gas, heated to treatment temperature and passed through a reactor containing a fixed bed of desulfurization catalyst. The hot reactor effluent exchanges heat with the incoming feed mixture and is cooled. The recycle hydrogen is separated from the liquid stream at high pressure, and recycled to the process to minimize makeup gas hydrogen requirements.

The liquid product stream is sent to a low pressure separator which allows the removal of dissolved gases before the next stage, a stripper column, where the product is freed from hydrogen sulfide and any light ends. Recycle hydrogen is also recovered from this low pressure separator. Part of the heat recovered from the reactor effluent stream may be used to supply heat to the product stripper reboiler or alternatively steam can be used.

All the processes are generally comparable and differ primarily in the type of catalyst used.

Technical Consideration

The hydrotreating (HT) of oil to remove sulfur is generally comparable in expense to flue gas desulfurization and the final selection depends on specific circumstances. This is generally true for fuel combustion uses. In FCC operation only part of the sulfur in the feed (2-30%) appears in the FCC regenerator flue gas. Thus, if feed desulfurization is carried out, it will be necessary to remove considerably more sulfur than is present in the FCC regenerator flue gas. However, hydrotreating of FCC feed to improve conversion, gasoline yield, and coke selectivity and run length has been a recognized process tool.¹⁵

The hydrotreating will likely be applied on the basis of improved yields or sulfur specifications in the FCC products rather than for SO_x standards on flue gas per se.

Hydrotreating of feed requires large amounts of hydrogen and it is assumed that a supply of hydrogen would be available in refineries--either from reformer off-gas or from a hydrogen plant.

TABLE III-3
DESULFURIZATION PROCESSES

<u>Process</u>	<u>Licensors</u>	<u>Operating Units</u>	<u>Total Distilled Capacity, BPSD</u>
1) Gulfining	Gulf Research & Development	6	7,000-8,000 (unit capacity)
2) Hydrofining	British Petroleum and Exxon	84	720,000
3) Hydrodesulfurization	Institute Francaise du Petrole	83	>1,000,000
4) Isomax	Chevron Research or UOP	25	900,000
5) Trickle Hydrosulfurization	Shell Development	82	1,050,000
6) HGO-Unicracking	Union Oil Co. of California		
7) Unifining	Union Oil Co. of California and UOP		
8) Gofining	Exxon R&E		

Source: The Oil and Gas Journal.

Other Pollution Problems

The hydrotreating of the feed to FCC results in the formation of H_2S . These gases are converted to sulfur in Claus-type units. There may be an aqueous waste stream, if the oil hydrotreated contains nitrogen. Also, water is often injected upstream of heat exchangers to prevent plugging.

Sulfur Removal Efficiency

The sulfur removal efficiency of hydrotreating may be as high as 97%. A sulfur removal efficiency of 90% is typical of economic operation. At this efficiency, the sulfur content of vacuum gas oil feed may be reduced to 0.3% (maximum 3.3% sulfur in feed to hydrotreater). Most of the sulfur compounds in the hydrotreated feed will be thiophenic in nature and a large portion of this sulfur will appear in the FCC regenerator flue gas. With 0.3% sulfur in the HT feed, the SO_x concentration in the flue gas will be 400-500 ppm. Thus, feed hydrotreating is not as effective a method as FGD to reduce SO_x in the FCC regenerator flue gas, if levels below 400-500 ppm are required.

The hydrotreating of feed can reduce NO_x emissions. However, the extent of this reduction is not known.

Status of Hydrotreating

The status of hydrotreating processes was presented in Table III-3. These processes are commercially proven.

E. ACHIEVABLE EMISSION LEVELS WITH BEST AVAILABLE CONTROL TECHNOLOGY

Achievable emission levels for SO_x and hydrocarbons with best available control technology are summarized in Table III-4 for a 50,000 BPSD FCC unit. The achievable level is 300 ppm for FGD based on 90% removal of SO_x from flue gas with a 3,000 ppm inlet concentration level. The corresponding level for hydrotreating the feed is 400-500 ppm based on desulfurization to 0.3 wt. % sulfur.

TABLE III-4

ACHIEVABLE EMISSION LEVELS WITH BEST CONTROL TECHNIQUES

FCC Plant Size - 50,000 BPSD (Total Feed)

<u>Significant Emission Point</u>	<u>Control Techniques</u>	<u>Achievable Emission Levels - PPM</u>		<u>Achievable Emission Rates - lb/hr</u>	
		<u>SO_x</u>	<u>Hydrocarbon</u>	<u>SO_x</u>	<u>Hydrocarbon</u>
Regenerator	FGD	300	500 ¹	400	167 ¹
	Feed Hydrotreating	400-500	500 ¹	670	167 ¹
	CO Boiler	900 ^{1 2}	10	1,200 ^{1 2}	3.4
	HTR	900	10	1,000	2.8 ³

¹Same as emission without control--represents average SO_x concentration and hydrocarbon emissions with no control.

²Based on projected national average for uncontrolled sources.

³Lower coke on catalyst with HTR produces less flue gas.

IV. STATE AND LOCAL AIR POLLUTION CONTROL REGULATIONS

As part of this study, we reviewed state and local air pollution regulations applicable to FCC regenerators. For reasons explained in Chapter III, the review of emission standards was limited to SO_x and hydrocarbons. The purpose of this chapter is to determine how the emission levels required by state and local regulations compare to the emission levels achievable with the control systems discussed in Chapter III.

A. SELECTION OF STATES FOR REVIEW OF REGULATIONS

In selecting states for consideration it was important to include a representative range of states. We reviewed the regulations for those seventeen states in which at least 1% (about 57,000 BPSD) of total U.S. FCC capacity was located. States falling into this category are shown in Table IV-1. As can be seen from Table IV-1, using this criteria we were examining state regulations governing 5,297,644 BPSD, or 93% of total U.S. capacity (fresh feed and recycle).

B. REGULATIONS

Table IV-2 shows the state regulations applicable to FCC's in the seventeen states examined.

Some of the states listed in Table IV-2 have SO_x emission standards in terms of ambient air quality or stack height. The application of these standards is naturally site-specific. To establish the existing SO_x emission baseline, an average emission standard was assigned to these states. This was accomplished by completing the weighted average of the SO_x emission standards applicable to states with source emission standards as shown in Table IV-3. It was assumed that this weighted average SO_x standard was representative of states having standards in terms of air quality or stack height and states not included in Table IV-2.

The SO_x emissions in the flue gas from FCC regenerators depend on feedstock, percent sulfur in the feedstock, and process variables. The affect of these variables are discussed in Chapter II. The typical SO_x concentration in the regenerator flue gas (Table II-2) is 800-900 ppm. However, the emissions may be as high as 1,500-2,500 ppm. A few states regulate SO_x emissions to 500 ppm or less. The remaining states have no SO_x emission regulation, or control it to 2,000 ppm. Flue gas desulfurization (FGD) systems and hydrotreating units have economic sulfur removal efficiency up to 90%. The SO_x emissions from FGD systems range from 50-300 ppm (depending on inlet SO_x concentration). The SO_x emissions from FCC regenerators using hydrotreated oil (0.3% S) range from 400-500 ppm. Thus, the states having stringent regulations may force the FCC regenerator owners to use low sulfur feedstocks (blended or hydrotreated) or to desulfurize the flue gas. Obviously, states having an SO_x emission standard equal to 2,000 ppm have less control. The reduction in emissions from state regulations levels achievable with existing control technology are shown in Table IV-4 for a typical FCC unit.

TABLE IV-1

STATES WITH FCC CAPACITY OF 1% OR GREATER

<u>PAD District</u>	<u>State</u>	<u>No. of Refineries With FCC's</u>	<u>Capacity (Fresh Feed and Recycle) (BPSD)</u>
1	Delaware	1	77,000
	New Jersey	4	269,444
	Pennsylvania	4	224,300
2	Illinois	9	523,277
	Indiana	4	203,800
	Kansas	10	206,450
	Minnesota	3	74,500
	Ohio	6	248,500
	Oklahoma	10	231,675
3	Louisiana	9	677,728
	Mississippi	2	76,850
	Texas	30	1,527,571
4	Montana	4	72,500
	Utah	6	70,160
	Wyoming	7	74,078
5	California	13	621,211
	Washington	3	118,600
Total		125	5,297,644

Source: The Oil and Gas Journal, March 29, 1976.

TABLE IV-2
STATE AIR REGULATIONS

<u>PAD District</u>	<u>State</u>	<u>SO_x</u>	<u>Hydrocarbons</u>
1	Delaware	Ambient ¹	None
	New Jersey	2,000 ppm ^{2a}	Ambient ¹
	Pennsylvania	500 ppm	None
2	Illinois	2,000 ppm	100 ppm equivalent methane (molecular weight 16.0)
	Indiana	$E_p = 19.5P^{0.673, 4}$	Waste gas stream to be burned in direct-flame afterburner or boiler
	Kansas	(County regulation)	
	(Kansas City)	None	None
	(Wichita)	--	--
	Minnesota	None	None
	Ohio	Existing - 2,000 ppm New - 500 ppm	None
	Oklahoma	Ambient ¹	None
3	Louisiana	Existing - 2,000 ppm	None
	Mississippi	Existing - 2,000 ppm New - 500 ppm	None
	Texas	440 ppm	Waste gas stream burned at 1,300°F or greater in a direct-flame incinerator or boiler
4	Montana	None	None
	Utah	Ambient ¹	None
	Wyoming	Ambient ¹	None
5	California	(County regulation)	
	(LA County)	2,000 ppm ^{2b}	85% reduction ⁵
	Washington	1,000 ppm	Ambient ¹

¹ Ambient air quality standard only.

^{2a} Also regulation on SO_x from fuel burned 310 ppm by volume adjusted to 12% CO₂ by volume (non-commercial fuel).

^{2b} Also regulation on sulfur content of fuel 0.5% sulfur by weight.

³ E_p = Emissions in pounds of SO₂/hour.

P = Tons of process weight/hour.

⁴ Indiana also regulates maximum hourly ground level concentrations in various air pollution regions of the state. The regulation is expressed as a formula involving:

S_p = Pounds of sulfur emitted/ton of process weight input.

n = Number of stacks.

a = Plume rise factor of 0.7.

h_s = Stack height in feet.

P = Total process equipment capacity weight input, tons/hour.

$$C_{max} = \frac{40 S_p P^{0.75} n^{0.25}}{a h_s}$$

⁵ Hydrocarbon emissions not to exceed 15 lb/day or 3 lb/hour.

TABLE IV-3

STATE AIR POLLUTION STANDARD FOR
SO_x EMISSIONS FROM FCC REGENERATOR

<u>State</u>	<u>FCC Capacity % of Total Capacity</u>	<u>Emission Standard Existing Source ppm in Flue Gas</u>	<u>Emission Standard New Source ppm in Flue Gas</u>
New Jersey	4.75	2,000	2,000
Pennsylvania	3.95	500	500
Illinois	9.22	2,000	2,000
Indiana	3.59	720 ¹	720 ¹
Ohio	4.38	2,000	500
Louisiana	11.94	2,000	2,000
Mississippi	1.35	2,000	500
Texas	26.92	440	440
Washington	2.09	1,000	1,000
California	<u>10.95</u>	<u>2,000</u>	<u>2,000</u>
Total	79.14		
Weight Average		1,337	1,227

¹Based on average size of FCC capacity in the State of Indiana.

Two states, Indiana and Texas, require combustion of flue gas at a certain temperature (usually 1,300°F) to control hydrocarbon emissions. Residence times on the order of 0.3 sec are also required. The hydrocarbon emissions from combustion of flue gas are usually lower than 10 ppm. Two other states regulate hydrocarbon emissions from FCC regenerators (see Table IV-5). States with regulations contain 40% of the FCC capacity. No hydrocarbon emission regulations were assumed in the remaining states.

The FCC units with CO boilers have very low hydrocarbon emissions. This is apparently also true for units employing HTR technology, although stack test results are scanty (Appendix A). The best practicable technology to control hydrocarbon emissions is to employ HTR or CO boilers as mentioned in Chapter III. It is estimated that only 28% of the FCC capacity will not be equipped with either of the above two options in 1975 (Chapter V). The effective emission level under state regulations (only a few states have hydrocarbon regulations) and best practicable technology are the same in this case.

TABLE IV-4

SO_x AND HDYROCARBON EMISSION REDUCTION
FROM TYPICAL PLANT BASED ON ACHIEVABLE CONTROL

FCC Plant Size - 50,000 BPSD (Total Feed)

<u>Emission Source</u>	<u>Control Technique</u>	<u>Emission Rate w/Achievable Control lb/hr</u>		<u>Emission Rate w/State-Required Control (Average) lb/hr</u>		<u>Emission Reduction By Applying Achievable Control lb/day</u>	
		<u>SO_x¹</u>	<u>Hydrocarbon²</u>	<u>SO_x</u>	<u>Hydrocarbon</u>	<u>SO_x</u>	<u>Hydrocarbon</u>
63 Regenerator	FGD	400	167	1,200	167	19,200	0
	Feed Hydrotreating	670 ²	167	1,200	167	12,720	0
	CO Boiler	1,200	3.4	1,200	167	0	3.926
	HTR	1,000	2.8	1,000	167	0	3,941

¹SO_x expressed as SO₂.

²Based on 500 ppm SO₂ in regenerator flue gas consistent with 'economic' removal to 0.3% S in FCC feed.

TABLE IV-5

STATE REGULATIONS FOR HYDROCARBON EMISSIONS

<u>State</u>	<u>Capacity (Fresh Feed and Recycle) (BPSD)</u>	<u>Control Level (ppm)</u>
Illinois	523,277	100
Indiana	203,800	10 (from incinerator)
Texas	1,527,571	10 (from incinerator)
Wisconsin	<u>10,700</u>	85% removal
Total	2,265,348*	

*2,265,348 BPSD represents 40% of total U.S. FCC capacity.

V. ESTIMATED EMISSION REDUCTIONS

Several models have been developed by the EPA for the determination of regulatory priorities over the past few years. The TRC Model IV, which is applied here, provides a quantitative estimate of the anticipated impact of standards of performance in preventing atmospheric emissions.

The additional control potential of new or revised standards of performance stems from the application of emission standards that are more stringent than those presently applied to construction and modification. This potential for a specified time period is expressed as $(T_S - T_N)$ where

T_S = emissions under 1975 state control regulations (tons/yr)

T_N = emissions under new or revised standards of performance (tons/yr)

To calculate the control potential of standards of performance, other factors must be considered such as total growth in capacity, the portion of growth requirements that can be satisfied from present unused capacity, and the obsolescence and replacement rates of existing facilities. TRC Model IV is a mathematical relationship incorporating these parameters, which can be used to determine the quantity $(T_S - T_N)$.

A detailed description of Model IV is provided in Appendix E. Parameters requiring quantitative information are defined below.

A. MODEL IV PARAMETERS

1. Parameter Definitions

T_U = total emissions in the impact year assuming no control (tons/yr)

T_A = total emissions in baseline year under baseline year regulations (tons/yr)

K = normal fractional utilization rate of existing capacity, assumed constant during time interval

A = baseline year production capacity (production units/yr)

P_C = construction and modification rate to increase industry capacity (decimal fraction of baseline capacity/yr)

P_B = construction and modification rate to replace obsolete capacity (decimal fraction of baseline capacity/yr)

C = production capacity from construction and modification to increase output above baseline year capacity (production units/yr)

B = production capacity from construction and modification to replace obsolete facilities (production units/yr)

E_{S1} = allowable emissions from existing sources under existing regulations (mass/unit capacity)

E_{S2} = allowable emissions from new and modified sources under existing regulations (mass/unit capacity)

E_N = allowable emissions from new sources under NSPS (mass/unit capacity)

2. Baseline Year

The model is applied to quantitatively estimate the emission reduction due to the enforcement of anticipated standards. The pollutants of concern are hydrocarbons and oxides of sulfur, for which there are no NSPS at present. The baseline year of 1975 is used to determine the effect of best control technology. The model is used to estimate the effect of anticipated NSPS over the period of ten years from 1975 to 1985. Therefore, 1985 is the impact year.

The numerical values assigned to the parameters are discussed below.

K - A value of 0.97 was used based on typical operating experience (see discussion in Chapter I).

A - The baseline FCC production capacity of 5,670 KBPSD (2069.6 MBPY)* is based on the latest Oil and Gas Journal refinery survey and represents the existing capacity at the end of 1975.

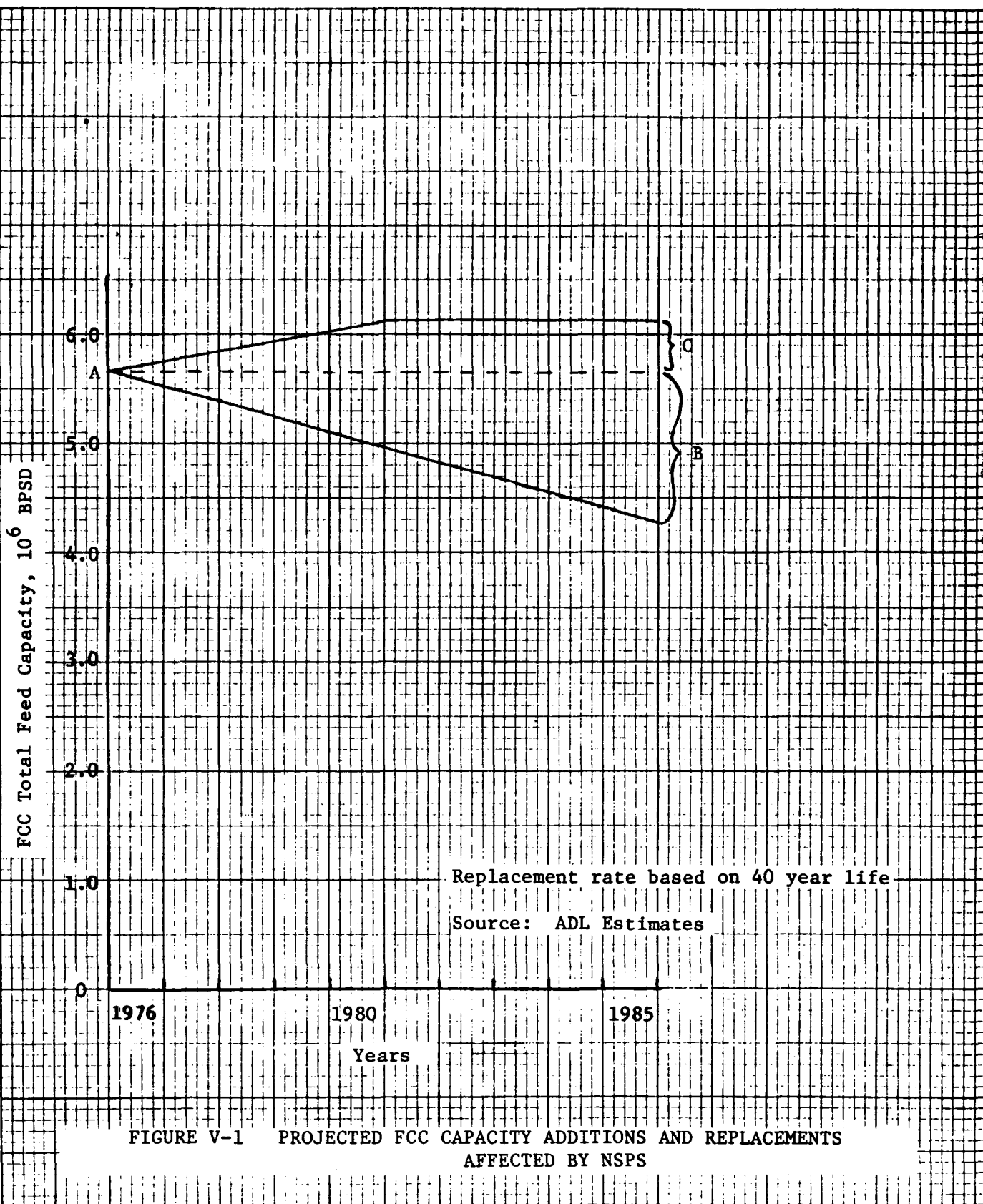
P_C - The compound rate of capacity growth through 1980 is 0.015 (decimal fraction of 1975 baseline capacity). Thereafter, P_C is assumed to be negligible (0.0). The basis for these projections is discussed in Chapter I.

P_B - The simple rate or replacement of obsolete capacity used in the calculation is 0.025 (decimal fraction of 1975 baseline capacity). This is based on an estimated 40-year equipment life which is more than twice the IRS depreciation life of 16 years. However, there are FCC units still operating that were built during World War II. Considering present uncertainties regarding energy policy and oil company devestiture, most refiners will continue to repair existing units in the short-term future.

B&C - The FCC capacity ultimately affected by NSPS was established by using the above factors to construct Figure V-1. The values of B and C at the end of the ten-year study period are 1,420 KBPSD (356.2 MBPY) and 440 KBPSD (160.6 MBPY), respectively. There are no FCC capacity additions assumed after 1980. The replacement of obsolete capacity is based on a 2.5% simple growth rate using the 1975 capacity as a basis.

*K = thousand

M = million



Values for the following parameters are specific to the pollutant being assessed.

- E_U - The uncontrolled SO_x emission factors were obtained from the knowledge of FCC capacity in each state, feed hydrotreating capacity in each state, sulfur content of feedstocks, the mix of oil feedstocks used in each PAD district, and relationship between SO_x in the regenerator flue gas and sulfur content in the feed. The details of this calculation are given in section B of this chapter. The E_U obtained for SO_x are 502 and 551 lb/1,000 barrels in 1975 and 1985, respectively. The corresponding values of E_U for hydrocarbons are 23.0 and 11.5 lb/1,000 barrels. The decline in emissions is due to increased use of HTR between 1975 and 1985.
- E_S - The emission factors under existing regulations were obtained by applying state regulations to emissions obtained from the uncontrolled sources in each state. The details of this calculation are also given in section B. The E_S obtained for SO_x is 401 lb/1,000 barrels in 1975. The values of E_{S1} and E_{S2} are 445 and 439 lb/1,000 barrels in 1985. The E_S values for hydrocarbons are the same as E_U since few states have standards and many units already have CO boilers.
- E_N - The SO_x emission factors under best control technology were obtained for two cases: 1) outlet SO_x concentration limited to 300 ppm, and 2) outlet SO_x concentration limited to 500 ppm. Necessary correction factors were applied to emission factors in some cases where the existing state emission regulations were lower than the above concentrations. The E_N equivalent to the above SO_x control levels are 182 and 290 lb/1,000 barrels. The E_N for hydrocarbons is 1.56 lb/1,000 barrels (as methane) based on typical emissions from CO boilers and HTR.

B. APPLICATION OF THE MODEL

The model is applied to determine emission reduction of SO_x and hydrocarbon pollutants. Since some parameters defined earlier are different for each pollutant, the application of the model to SO_x emissions and to hydrocarbon emissions are discussed separately.

1. Application of TRC Model IV to SO_x Emissions

In applying the model to determine the impact of NSPS for SO_x we accounted for various factors that affect the sulfur emission from FCC regenerators. These include:

1. variations in FCC feed sulfur content by geographic region and time,
2. incidence of feed hydrodesulfurization,
3. recycle ratio, and
4. existing state emission regulations.

The use of these factors to develop E_U , E_S , and E_N are discussed next followed by the calculation of total emissions of SO_x and $T_N - T_S$.

a. SO_x Concentration in Flue Gas from FCCU Regenerators

The regenerator outlet SO_x concentrations shown in Table V-1 are based on the correlation presented in Figure V-2.²⁰ In Figure V-2, the outlet SO_x concentration is related to sulfur content of the feedstock for different types of feed. This relationship is based on 2% excess oxygen in the flue gas. The SO_x emissions in the flue gas from regenerators for the case of hydrotreated feed were also obtained from Figure V-2 and are consistent with other literature.^{24, 22} The average sulfur content of hydro-treated feeds was assumed at 0.3%, to be consistent with economic desulfurization levels.

In each PAD district, the blend of gas oil feeds to the FCC differs. This is shown in Table V-2. The mix also varies with time, and the breakdown by source is given for the years 1975 and 1985. The mix does not include hydrotreated oil; this is dealt with separately in the preceding sections. The average SO_x concentrations in the regenerator flue gas for each PAD district is obtained by weighting the emission data in Table V-1.

In FCC operation, part of the light cycle oil is recycled. An average recycle rate equal to 10% of the total FCC feed was assumed. In Table V-3, SO_x emissions from the recycle oil are developed based upon 100% recycle oil. The average weight percent sulfur in FCC fresh feed was obtained from the type of mix (Table V-2) and the sulfur content in different types of gas oils (Table V-1). The weight percent sulfur in the recycle oil was obtained from a published correlation of sulfur content in the light cycle oil and sulfur content of FCC feed.²⁰ The SO_x concentrations in the flue gas from the recycle oil was then estimated using Figure V-3.

The estimated average SO_x concentrations in the flue gas from FCC regenerators for each state are given in Table V-4 with appropriate weighting for fresh, recycle and hydrotreated feeds. The SO_x concentrations are given for the years 1975 and 1985. The distribution of FCC and hydrotreating capacity in each state was assumed to be constant over the period 1975 to 1985. The 1975 FCC and the hydrotreating capacities were obtained from a recent survey.⁹ An SO_x concentration equal to the average SO_x concentration was used to fill the data gap (PAD District IV, 4.2% FCC capacity).

b. SO_x Emissions with No Control, E_U , SO_x

The average uncontrolled SO_x concentrations from FCC regenerators including the contributions from recycle and desulfurized feeds are given in Tables V-5 and V-6. The percent capacity in each state and the SO_x concentrations in the effluent were obtained from Table V-4.

It is necessary to have a relationship between flue gas flow rate and oil feed to FCC units to convert SO_x concentrations to emission factors. The coke yield varies with the severity of cracking. A coke yield equal

TABLE V-1

**SO_x CONCENTRATION IN FLUE GAS FROM FCC REGENERATORS
FOR DIFFERENT CRUDES**

Crude Code¹	S in FCC Feed (%)	SO_x in Outlet Flue Gas, ppm²
L	0.237	300
T	1.659	1,300
N	0.269	400
A	1.925	2,100
V	1.374	1,250
O	0.202	300
MC	0.613	500
AL	0.17	280
CW	1.22	450
CV	1.434	480
I	0.078	175
ANS	0.885	1,000
HDS	0.3	450
HDS Recycle	0.5	800

¹See Chapter I for explanation of code. HDS refers to hydrodesulfurization oil.

²Outlet flue gas O₂ concentration = 2%.

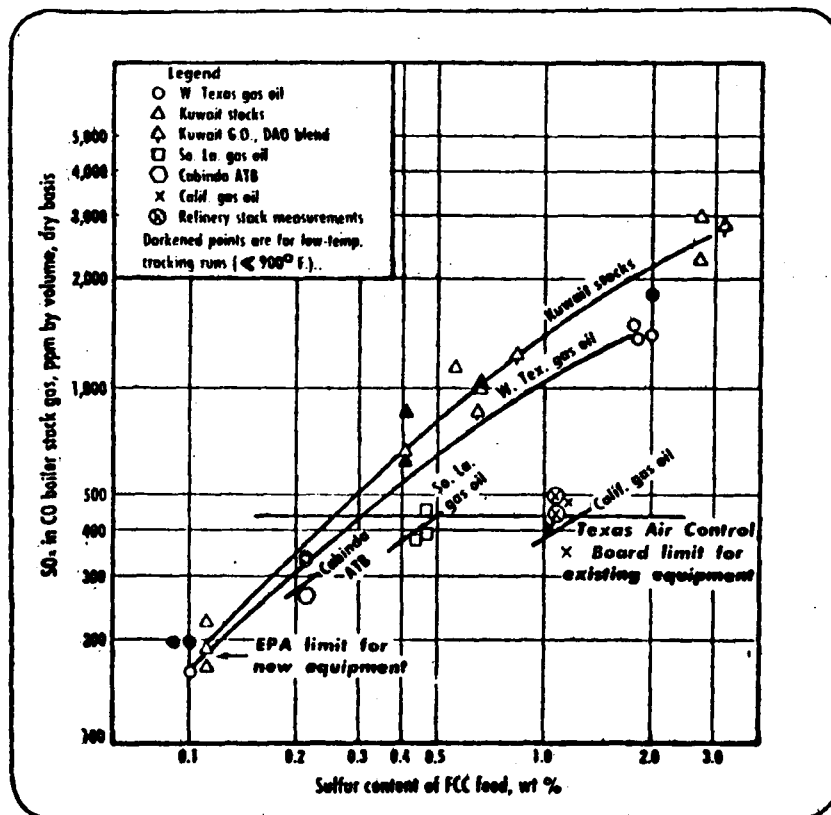


FIGURE V-2 SO_x CONTENT OF CO BOILER STACK GAS*

*Assuming no supplementary fuel to the boiler and 2.0% oxygen in boiler stack gas.

Source: Gulf R&D.²⁰

TABLE V-2

SO_x CONCENTRATION IN FLUE GAS FROM FCC REGENERATOR

PAD District ¹	Type of Crude ¹	Crude Volume Percent ¹		Average SO _x Concentration in Outlet, ppm ²	
		1975	1985	1975	1985
I	L	15.4	--	825	1,300
	N	16.2	19.2		
	T	7.6	--		
	A	7.6	45.7		
	V	31.7	16.5		
	AL	21.5	18.6		
IIa	L	7.6	--	465	700
	T	13.1	10.0		
	O	61.5	55.8		
	MC	17.8	--		
	A	--	17.1		
	AL	--	17.1		
IIb	L	6.0	--	1,175	1,575
	T	70.3	55.1		
	O	4.9	4.4		
	A	8.5	40.5		
	MC	10.3	--		
IIIa	L	88.7	88.2	415	425
	T	11.3	11.8		
IIIb	L	47.4	47.4	825	825
	T	41.4	41.4		
	N	3.8	3.8		
	A	5.3	5.3		
	V	2.1	2.1		
V	CW	37.4	40.0	945	700
	CV	13.8	13.2		
	A	31.3	--		
	MC	7.1	--		
	I	10.4	--		
	ANS	--	46.8		

¹See Chapter I for details.²The SO_x concentrations in the flue gas are based on no hydrotreating of feed to catalytic reactor. The SO_x concentrations are based on 2% O₂ concentration in flue gas from FCC regenerator system.

TABLE V-3
SO_x EMISSIONS FROM RECYCLE OIL
 (100% Basis)

PAD District*	Wt. % S in FCC Feed		Wt. % S in Recycle Oil		SO _x Concentration in Emissions	
	1975	1988	1975	1988	1975	1988
I	0.82	1.19	1.10	1.75	1,025	1,250
IIa	0.47	0.64	0.74	0.90	875	1,000
IIb	1.42	1.70	2.02	2.40	1,400	1,650
IIIa	0.40	0.41	0.70	0.70	800	800
IIIb	1.54	1.54	2.20	2.20	1,500	1,500
V	1.31	1.09	1.92	1.50	1,300	1,200

*See Chapter I for details on classification by PAD Districts.

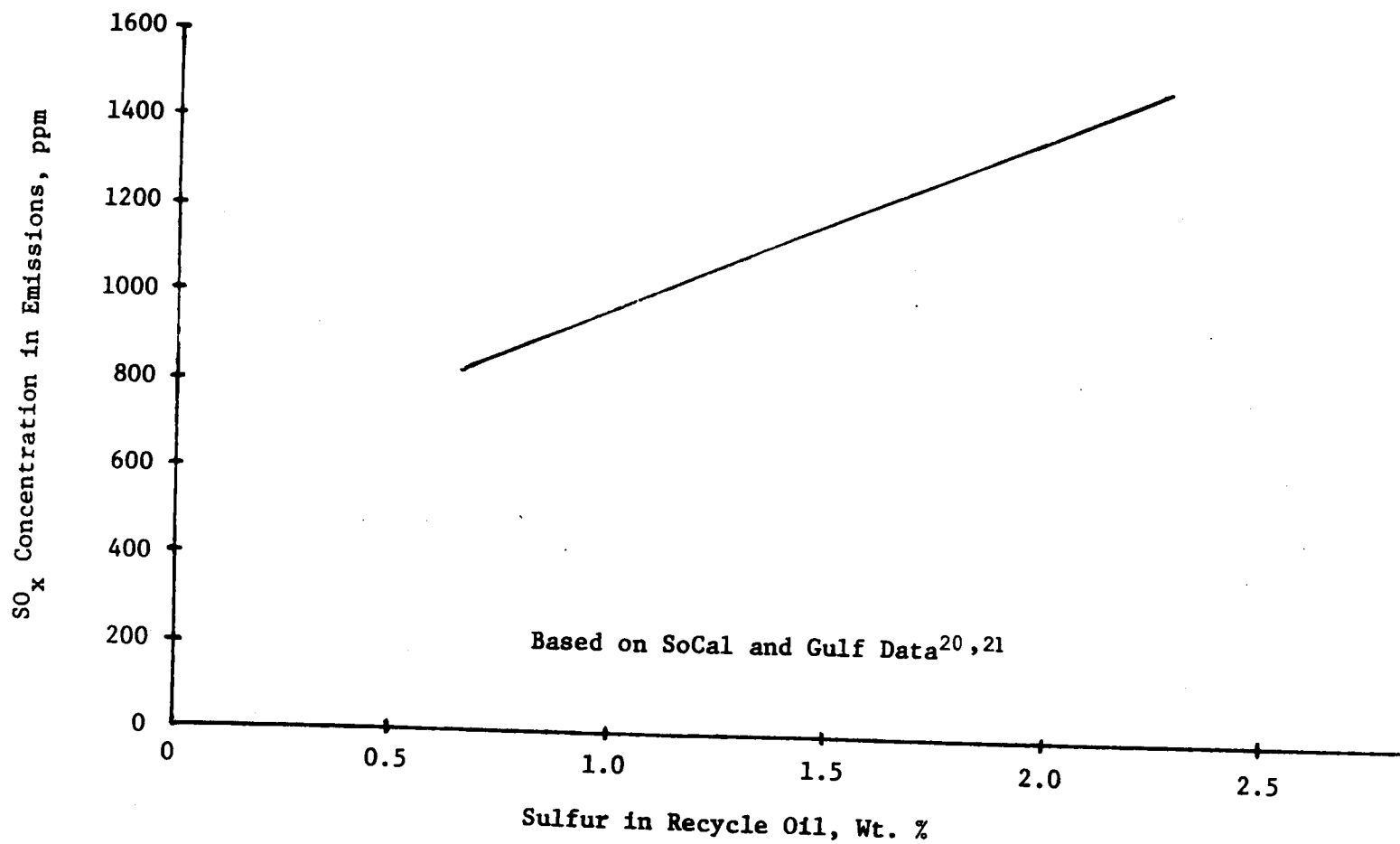


FIGURE V-3 SO_x EMISSIONS ATTRIBUTABLE TO SULFUR IN RECYCLE OILS

TABLE V-4

SO_x CONCENTRATION IN UNCONTROLLED EMISSIONS

<u>PAD District</u>	<u>State</u>	<u>Capacity BPSD (1975)</u>	<u>SO_x Concentration in Flue Gas</u>		
			<u>(1975)</u>	<u>(1985)</u>	
I	Delaware				
	Fresh	69,300	745	1,170	
	Recycle	7,700	105	125	
	Total	77,000		850	1,295
	New Jersey				
	Fresh	242,500	745	1,170	
	Recycle	26,944	105	125	
	Total	269,444		850	1,295
	New York				
	Hydrotreating	20,000	190	190	
	Recycle	2,200	40	40	
	Fresh	22,300	390	615	
	Recycle	2,500	55	65	
	Total	47,000		675	910
	Pennsylvania				
	Hydrotreating	40,000	80	80	
	Recycle	4,400	15	15	
	Fresh	161,870	595	940	
	Recycle	18,030	85	100	
	Total	224,300		775	1,135
	Virginia				
	Fresh	28,800	745	1,170	
	Recycle	3,200	105	125	
	Total	32,000		850	1,295
II (Large)	Illinois				
	Hydrotreating	27,000	25	25	
	Recycle	3,000	5	5	
	Fresh	443,950	1,000	1,335	
	Recycle	49,327	135	155	
	Total	523,277		1,165	1,520
	Indiana				
	Fresh	183,420	1,060	1,420	
	Recycle	20,380	140	165	
	Total	203,800		1,200	1,585

TABLE V-4 cont'd

PAD District	State	Capacity BPSD	SO _x Concentration in Flue Gas		
		(1975)	(1975)	(1985)	
	Kentucky				
	Fresh	49,500	1,060	1,420	
	Recycle	5,500	140	165	
	Total		1,200		1,585
		55,000			
	Michigan				
	Hydrotreating	12,500	120	120	
	Recycle	1,390	25	25	
	Fresh	29,710	745	995	
	Recycle	3,300	100	115	
	Total		990		1,255
		46,900			
	Tennessee				
	Fresh	12,150	1,060	1,420	
	Recycle	1,350	140	165	
	Total		1,200		1,585
		13,500			
II (Small)	Kansas				
	Fresh	185,800	420	630	
	Recycle	20,650	90	100	
	Total		510		730
		206,450			
	Minnesota				
	Hydrotreating	20,000	120	120	
	Recycle	2,200	25	25	
	Fresh	47,050	295	440	
	Recycle	5,250	60	70	
	Total		500		655
		74,500			
	Missouri				
	Fresh	47,700	420	630	
	Recycle	5,300	90	100	
	Total		510		730
		53,000			
	Nebraska				
	Fresh	2,610	495	630	
	Recycle	290	90	100	
	Total		510		730
		2,900			
	North Dakota				
	Fresh	30,600	420	630	
	Recycle	3,400	90	100	
	Total		510		730
		34,000			

TABLE V-4 cont'd

PAD District	State	Capacity BPSD (1975)		SO _x Concentration in Flue Gas		
				(1975)	(1985)	
IIIa	Oklahoma					
	Fresh	208,507		420	630	
	Recycle	23,168		90	100	
	Total		231,675	510		730
	Wisconsin					
	Fresh	9,630		420	630	
	Recycle	1,070		90	100	
	Total		10,700	510		730
	Ohio					
	Hydrotreating	22,500		40	40	
	Recycle	2,500		10	10	
	Fresh	201,150		375	565	
	Recycle	22,350		80	90	
	Total		248,500	505		705
	Arkansas					
	Fresh	16,200		375	385	
	Recycle	1,800		80	80	
	Total		18,000	455		465
	Louisiana					
	Hydrotreating	41,000		30	30	
	Recycle	4,560		5	5	
	Fresh	568,960		350	355	
	Recycle	63,210		75	75	
	Total		677,730	460		465
	Mississippi					
	Hydrotreating	23,000		135	135	
	Recycle	2,560		25	25	
	Fresh	46,170		250	255	
	Recycle	5,130		55	55	
	Total		76,850	465		470
IIIb	New Mexico					
	Fresh	15,800		740	745	
	Recycle	1,760		150	150	
	Total		17,560	890		895
	Texas					
	Hydrotreating	70,000		20	20	
	Recycle	7,800		5	5	
	Fresh	1,304,810		705	705	
	Recycle	144,960		140	140	
	Total		1,527,571	870		870

TABLE V-4 cont'd

PAD District	State	Capacity BPSD (1975)		SO _x Concentration in Flue Gas		
				(1975)	(1985)	
IV	Colorado					
	Fresh	21,500		725	820	
	Recycle	2,400		80	90	
	Total		23,900		805	910
	Montana					
	Fresh	65,250		725	820	
	Recycle	7,250		80	90	
	Total		72,500		805	910
	Utah					
	Fresh	63,144		725	820	
	Recycle	7,016		80	90	
	Total		70,160		805	910
	Wyoming					
	Hydrotreating	16,000		190	195	
	Recycle	1,780		20	20	
	Fresh	50,670		550	625	
	Recycle	5,630		60	70	
	Total		74,078		805	910
V	California					
	Hydrotreating	58,000		40	40	
	Recycle	6,400		10	10	
	Fresh	501,090		760	565	
	Recycle	55,721		120	105	
	Total		621,211		930	720
	Hawaii					
	Fresh	20,700		850	630	
	Recycle	2,300		130	120	
	Total		23,000		980	750
	Washington					
	Hydrotreating	8,500		35	35	
	Recycle	940		5	5	
	Fresh	98,240		785	580	
	Recycle	10,920		120	110	
	Total		118,600		945	730

TABLE V-5

ESTIMATED SO_x EMISSIONS FROM FCC IN 1978

<u>PAD District</u>	<u>State</u>	<u>Percent Capacity</u>	<u>Uncontrolled SO_x Emissions</u>		<u>Emissions Existing Regulations</u>
			<u>ppm</u>	<u>tons/yr</u>	<u>tons/yr</u>
I	Delaware	1.36	850	7,499	7,499
	New Jersey	4.75	850	26,191	26,191
	New York	0.83	675	3,634	3,634
	Pennsylvania	3.95	775	19,858	12,812
	Virginia	0.32	850	1,765	1,765
II (Large)	Illinois	9.22	1,165	69,679	69,679
	Indiana	3.59	1,200	27,946	16,768
	Kentucky	0.97	1,200	7,551	{7,551 7,923 ¹
II (Small)	Kansas	3.64	510	12,043	585
	Michigan	0.83	990	5,330	5,330
	Minnesota	1.31	500	4,249	4,249
	Missouri	0.93	510	3,077	3,077
	Nebraska	0.05	510	165	165
	North Dakota	0.60	510	1,985	1,985
	Ohio	4.38	505	14,349	{14,349 14,580 ¹
	Oklahoma	4.08	510	13,498	13,498
	Tennessee	0.24	1,200	1,868	1,868
	Wisconsin	0.19	510	629	629
	Arkansas	0.32	455	945	945
III	Louisiana	11.94	460	35,629	35,629
	Mississippi	1.35	465	4,072	4,072
	New Mexico	0.31	890	1,790	1,790
	Texas	26.92	870	151,928	76,837
IV	Colorado	0.42	805	2,193	2,193
	Montana	1.28	805	6,684	6,684
	Utah	1.24	805	6,475	6,475
	Wyoming	1.31	805	6,841	6,841
V	California	10.95	930	66,060	66,060
	Hawaii	0.41	980	2,607	2,607
	Washington	2.09	945	12,812	{12,812 17,073 ¹
				519,352	{414,579 ² 463,769 ³

¹Emissions under state new source regulations assuming all capacity affected.

²Total emissions from all sources with existing source regulations.

³Total emissions from all sources with new source regulations. Note that for some states the new and existing source regulations are identical.

The SO_x emissions are reported as SO₂.

TABLE V-6

ESTIMATED SO_x EMISSIONS FROM FCC IN 1985

State	Percent Capacity	Uncontrolled SO _x Emissions		Emissions with Existing State Regulations	Emissions if SO _x in All Flue Gas is ⁴	
		ppm	tons/yr		≥300 ppm tons/yr	≥500 ppm tons/yr
Delaware	1.36	1,295	11,940	{11,940 11,313 ¹	2,766	4,610
New Jersey	4.75	1,295	41,703	41,703	9,661	16,102
New York	0.83	910	5,121	5,121	1,688	2,814
Pennsylvania	3.95	1,135	30,395	13,390	8,034	13,390
Virginia	0.32	1,295	2,809	{2,809 2,661 ¹	651	1,085
Illinois	9.22	1,520	95,012	95,012	18,752	31,254
Indiana	3.59	1,585	38,577	17,524	7,302	12,169
Kansas	3.64	730	18,015	18,015	7,403	12,339
Kentucky	0.97	1,585	10,423	{8,792 8,069 ¹	1,973	3,288
Michigan	0.83	1,255	7,062	{7,062 6,904 ¹	1,688	2,814
Minnesota	1.31	655	5,817	5,817	2,664	4,440
Missouri	0.93	730	4,603	4,603	1,892	3,153
Nebraska	0.05	730	247	247	102	169
North Dakota	0.60	730	2,969	2,969	1,220	2,034
Ohio	4.38	705	20,935	{20,935 14,848 ¹	8,909	14,848
Oklahoma	4.08	730	20,192	20,192	8,298	13,830
Tennessee	0.24	1,585	2,579	2,579	488	814
Wisconsin	0.19	730	940	940	386	644
Arkansas	0.32	465	1,009	1,009	651	1,009
Louisiana	11.94	465	37,641	37,641	24,285	37,641
Mississippi	1.35	470	4,302	4,302	2,746	4,302
New Mexico	0.31	895	1,881	1,881	631	1,051
Texas	26.92	870	158,781	80,303	54,752	80,303
Colorado	0.42	910	2,591	2,591	854	1,424
Montana	1.28	910	7,897	7,897	2,609	4,339
Utah	1.24	910	7,650	7,650	2,522	4,203
Wyoming	1.31	910	8,082	8,082	2,664	4,441
California	10.95	720	53,450	53,450	22,271	37,119
Hawaii	0.41	750	2,085	2,085	834	1,390
Washington	2.09	730	10,344	10,344	4,251	7,085
			615,052	496,885 ²	202,947	324,104
				489,142 ³		

¹Emissions under state new source regulations assuming all capacity affected.

²Total emissions from all sources with existing source regulations.

³Total emissions from all sources with new source regulations. Note that for some states the new and existing source regulations are identical. The SO_x emissions are reported as SO₂.

⁴Based on all capacity affected by NSPS. Used to calculate weighted average E_N, not ultimate impact.

to 6 percent and 5 percent is assumed for conventional regenerator and high temperature regenerator, respectively. The capacity of a FCC having HTR is assumed to be 15% for 1975 and 60% for 1985.

The air to coke mass ratio equal to 14.2 is used to determine the amount of flue gas with 2 percent excess oxygen. A flue gas to oil mass equal to 0.936 and 0.782 is obtained from the above bases for conventional regenerators and HTR, respectively. The average flue gas to oil ratio corresponds to 0.91 and 0.84 for the years 1975 and 1985, respectively.

The FCC capacity, SO_x concentrations in the flue gas, and mass ratio of flue gas to FCC feed oil are used to determine uncontrolled emissions in Tables V-5 and V-6. An FCC feed oil density equal to 315 lb/barrel is used in the above calculation. From Tables V-5 and V-6, the uncontrolled emissions (national average) in the years 1975 and 1985 are 519,352 ton/yr and 615,052 ton/yr, respectively. The emission factor calculated from this is 501.9 lb/1,000 barrels (805 ppm) in 1975 and 551.6 lb/1,000 barrels (905 ppm) in 1985.

c. SO_x Emissions with Existing Regulations, E_S , SO_x

The state emission standards summarized in Chapter IV are used as existing standards. The emissions under existing regulations for FCC's are developed in Tables V-5 and V-6. The emissions shown represent the lesser of the uncontrolled emissions or allowed emissions. The determination of allowable emissions was obtained from allowable SO_x concentration in the flue gas (see Chapter IV), mass ratio of flue gas to oil feed to FCC, and the capacity of FCC. The total estimated SO_x emissions (ton/yr) under existing regulations are shown in Tables V-5 and V-6. The calculated emission factors E_S (1975), E_{S_1} (1985), and E_{S_2} (1985) are 400.7, 445.6, and 438.7 lb/1,000 barrels, respectively.

Here, E_{S_1} (1985) refers to allowable (national average) SO_x emissions under existing regulations for existing FCC's in the year 1985, E_{S_2} (1985) refers to allowable SO_x emissions allowing for weighting of those states which have different standards for new or modified FCC in the year 1985, and E_S (1975) refers to allowable emissions in the year 1975.

d. SO_x Emissions with Anticipated Regulations, E_N

The E_N is determined for two potential control levels: (1) 300 ppm SO_x and (2) 500 ppm SO_x in the flue gas. It may not be possible to use low sulfur oils without a FGD system to meet the 300 ppm standard. The 500 ppm level can very likely be achieved by using low sulfur oil (maybe hydrotreated) as FCC feed.

Since some states have emission regulations that fall below the 500 ppm level, a weighted average E_N was determined by calculating the total SO_x emission using the lesser quantity for each state and then dividing the total FCC capacity. The emission factors calculated from the total emissions given in Table V-6 are $E_{N,300} = 182$ lb/1,000 barrels oil and

$E_{N,500} = 290.7$ lb/1,000 barrels oil. It should be noted that $E_{N,500}$ corresponds to less than 500 ppm SO_x in the flue gas. This is because the SO_x regulations for some states are lower than 500 ppm.

e. Calculation of Total SO_x Emissions and Expected Reduction Due to NSPS

- Total SO_x emissions in 1975, T_A

$$\begin{aligned} T_A &= E_S \cdot K \cdot A \\ &= \frac{400.7}{1,000} \times 0.97 \times 5.67 \times 10^6 = 2,203,809 \text{ lb/day} \\ &= 402,195 \text{ ton/yr} \end{aligned}$$

- Total SO_x emissions in 1985, assuming no control, T_U

$$\begin{aligned} T_U &= E_U K(A+C) \\ &= \frac{551.6}{1,000} \times 0.97 \times (5.67 \times 10^6 + 0.44 \times 10^6) \\ &= 3,269,170 \text{ lb/day} \\ &= 596,620 \text{ ton/yr} \end{aligned}$$

- Total SO_x emissions in 1985 under existing standards, T_S

$$\begin{aligned} T_S &= E_{S_1} K(A-B) + E_{S_2} (B+C) \\ &= \frac{445.6}{1,000} \times 0.97(5.67 \times 10^6 - 1.42 \times 10^6) + \frac{438.7}{1,000} \times \\ &\quad 0.97(1.42 \times 10^6 + 0.44 \times 10^6) \\ &= 1,836,986 + 791,502 \text{ lb/day} \\ &= 479,699 \text{ ton/yr} \end{aligned}$$

- Total SO_x emissions in 1985 under anticipated NSPS, T_N

Two levels of NSPS are assumed: (1) 300 ppm and (2) 500 ppm.

$$\begin{aligned} T_{N,300} &= E_{S_1} K(A-B) + E_{N,300} K(B+C) \\ &= 1,836,986 + \frac{182}{1,000} \times 0.97(1.42 \times 10^6 + 0.44 \times 10^6) \\ &= 2,165,350 \text{ lb/day} \\ &= 395,176 \text{ ton/yr} \end{aligned}$$

Similarly, $T_{N,500} = 2,361,466 \text{ lb/day}$

$$T_{N,500} = 430,967 \text{ ton/yr}$$

- Emission Reduction Potential from 1975 to 1985

$$T_{N,300} - T_S = 84,523 \text{ ton/yr}$$

$$T_{N,500} - T_S = 48,732 \text{ ton/yr}$$

2. Application of TRC Model IV to Hydrocarbon Emission

In this section, the estimated reduction of hydrocarbon pollutants due to anticipated NSPS is calculated. Model IV is applied to hydrocarbons in the same way as it was applied to oxides of sulfur. The values of K, A, B, C, P_B and P_C are the same in both cases. A 1975 baseline year is used.

a. Hydrocarbon Emissions with No Control, E_U , Hydrocarbon

Hydrocarbon emissions from the conventional regenerators are <500 ppm. This is equivalent to 3,900 lb/day (calculated as methane) from a 50,000 BPSD FCC unit. Thus, the hydrocarbon emission factor for a conventional regenerator is 78 lb/1,000 barrel.

In 1975, 15% of the total FCC capacity was estimated to have HTR and 67% of the total FCC's capacity was estimated to have CO boilers. The hydrocarbon emissions in the flue gas from HTR or CO boilers is <10 ppm. The percent of FCC having both CO boilers and HTR is not available. By random distribution, the percentage of FCC's having CO boilers and HTR units is estimated as follows:

$$\text{Percent} = 100(0.15)(.67) = 10$$

Therefore, the percent of FCC's having CO boilers or HTR is $15 + 67 - 10 = 78$. The emission of hydrocarbon from uncontrolled units is 78 lb/day (calculated as methane) from a 50,000 BPSD FCC unit. Thus, the emission factor from HTR or CO boilers is 1/50th of this or 1.56 lb/1,000 barrels.

The average hydrocarbon emission factor for all FCC is $0.28(78) + 0.72(1.56)$ or 22.96 lb/1,000 barrels in 1975.

It is expected that the percent of HTR units will increase to 60 in 1985. Therefore, by the above procedure, 87 percent of the FCC's will be equipped with HTR or CO boilers. Thus, the hydrocarbon emission factor, E_U , is expected to decrease to 11.5 lb/1,000 barrels.

b. Allowable Hydrocarbon Emissions
Under Existing Regulations, E_S

The hydrocarbon emissions from FCC's are effectively controlled by HTR or CO boilers. HTR or CO boilers on the FCC's to increase the yield or to improve heat recovery. As shown in Table IV-4, 40 percent of FCC's are located in the states where hydrocarbon emissions are controlled. However, it is difficult to segregate FCC's which have installed HTR or CO boilers to meet pollution regulations or other reasons. However, the E_U was calculated based on an estimate of the national average population of CO boilers and FCC's with HTR. Thus,

$$E_S = E_U = 22.96 \text{ lb/1,000 barrels in 1975, and}$$

$$E_S = E_U = 11.5 \text{ lb/1,000 barrels in 1985.}$$

c. Allowable Hydrocarbon Emissions under
Standards of Performance, E_N

The best available control technology, BACT, for hydrocarbon emission reduction is the installation of HTR or a CO boiler in the FCC. Thus, the hydrocarbon concentration in the flue gas is <10 ppm; the hydrocarbon emission factor is 1.56 lb/1,000 barrels (calculated as methane).

d. Calculation of Total Hydrocarbon Emissions and $(T_S - T_N)$

- Total hydrocarbon emissions in 1975, T_A

$$T_A = E_S K A$$

$$= \frac{22.96}{1,000} \times 0.97 \times 5.67 \times 10^6 = 126,278 \text{ lb/day}$$

$$= 23,046 \text{ ton/yr}$$

Total hydrocarbon emissions in 1985 assuming no control, T_U

$$T_U = E_U K (A+C)$$

$$= \frac{11.5}{1,000} \times 0.97 (5.67 \times 10^6 + 0.44 \times 10^6)$$

$$= 68,157 \text{ lb/day}$$

$$= 12,439 \text{ ton/yr}$$

- Total hydrocarbon emissions in 1985 under existing standards, T_S

$$T_S = T_U = 12,439 \text{ ton/yr}$$

Total hydrocarbon emissions in 1988 under anticipated NSPS, T_N .

It is expected that all the new or modified FCC's will be equipped with HTR or CO boilers. Thus, $T_N = T_S = 12,439$ ton/yr.

- Emission Reduction

$$T_S - T_N = 0$$

It is expected that the NSPS for hydrocarbon emissions from FCC regenerators will have minimal effect.

C. IMPACT OF SULFUR AND HYDROCARBON NSPS FOR FCC REGENERATOR

The impact of NSPS for sulfur oxides and hydrocarbon emissions from FCC regenerators is summarized in Table V-7. The reduction in sulfur emissions by 1985 are 49,000 or 85,000 ton/yr depending on whether the control level is 500 or 300 vppm SO_x in the treated gas. The magnitude of the impact is small due to the relatively small growth rate of new capacity and the low rate of replacement of existing facilities. Another factor affecting the magnitude is that U.S. refineries run blended feedstocks from various crudes, which tends to reduce the average sulfur in the FCC feed on the national basis.

The impact of NSPS for hydrocarbons is expected to be negligible since it is unlikely that a new FCC unit would be built without either a CO boiler or the capability for HTR. Therefore, the practical NSPS level would be consistent with what would occur in any event. Stated mathematically, E_N is equal to E_{S_2} where E_{S_2} is the effective value not the statutory value, since by that time most new units would either have CO boilers or have been installed with HTR.

TABLE V-7
SUMMARY OF INPUT/OUTPUT VARIABLES
FOR MODEL IV

<u>Common Factors</u>				
	K		0.97	
	A (1975)		5.67×10^6 BPSD ¹	
	P _B		1.5% up to 1980 and 0 after	
	B (1985)		0.44×10^6 BPSD	
	P _C		2.5% of 1975 capacity	
	C (1985)		1.42×10^6 BPSD	

<u>Changing Factors</u>		<u>Units</u>	<u>SO_x</u>	<u>Hydrocarbon</u>
E _U	(1975)	lb/1,000 Barrel	502	22.96
E _U	(1985)	lb/1,000 Barrel	551	11.5
E _S	(1975)	lb/1,000 Barrel	401	22.96
E _{S1}	(1985)	lb/1,000 Barrel	445	11.5
E _{S2}	(1985)	lb/1,000 Barrel	439	11.5
E _N		lb/1,000 Barrel	182 ² or 290 ³	1.56
E _{S2}	(1985)	lb/1,000 Barrel	182 ² or 290 ³	1.56
T _A	(1975)	1,000 Ton/Yr	402	23
T _S	(1985)	1,000 Ton/Yr	480	12
T _N	(1985)	1,000 Ton/Yr	395 ² or 431 ³	12
T _S -T _N		1,000 Ton/Yr	85 ² or 49 ³	0

¹ 1 Barrel = 315 lb

² SO_x Outlet ppm 300

³ SO_x Outlet ppm 500

VI. MODIFICATION & RECONSTRUCTION

Fluid catalytic cracking technology as it exists today is a result of a series of evolutionary process improvements which have increased the yields and capacity of existing units. The significant developments which have been responsible for these improvements include:

- Introduction of zeolite catalysts and riser cracking, and
- Raising operating pressure.

In general, most older units have been modified to take advantage of the expansion opportunities available from the operating improvements listed above. Immediate projects do not indicate that another round of expansions based on catalyst improvements is imminent.

The airborne emissions from FCC units with conventional regeneration are directly related to the yield of coke which deposits on the catalyst and is removed by air oxidation (regeneration). The affect of process evolution on coke yield is clearly illustrated in Figure VI-1. The introduction of improved catalysts and regeneration techniques has reduced the coke yield at a given conversion level. However, it does not necessarily follow that the emissions from regeneration were similarly reduced. The major advantage of these process improvements was that conversion could be increased for a given amount of coke on the catalyst. Therefore, in practice the coke yields and hence the emissions would not have been greatly reduced by past improvements (high temperature regeneration excepted).

The most recent FCC technology development is complete combustion of CO from catalyst regeneration, otherwise known as high temperature regeneration (HTR) or in-situ CO combustion. The objective is to obtain more complete combustion of the coke on the catalyst. Both thermal and catalytic methods are used to induce the oxidation reactions. The major benefits of the process include:

- Increased catalyst activity due to improved regeneration (reduced coke), and
- Reduced CO emissions.

Because for a given set of conditions, there is less coke on the catalyst with HTR, cracking severity or oil/catalyst ratios can be increased. The result in the first case is to improve the yields of gasoline and distillate from a given amount of feed, and in the second case to increase the fresh feed capacity. Hence, there are economic incentives which accrue to HTR in addition to the reduction of CO emissions. Hence, revamping FCC units for HTR is the current trend in technology improvements.

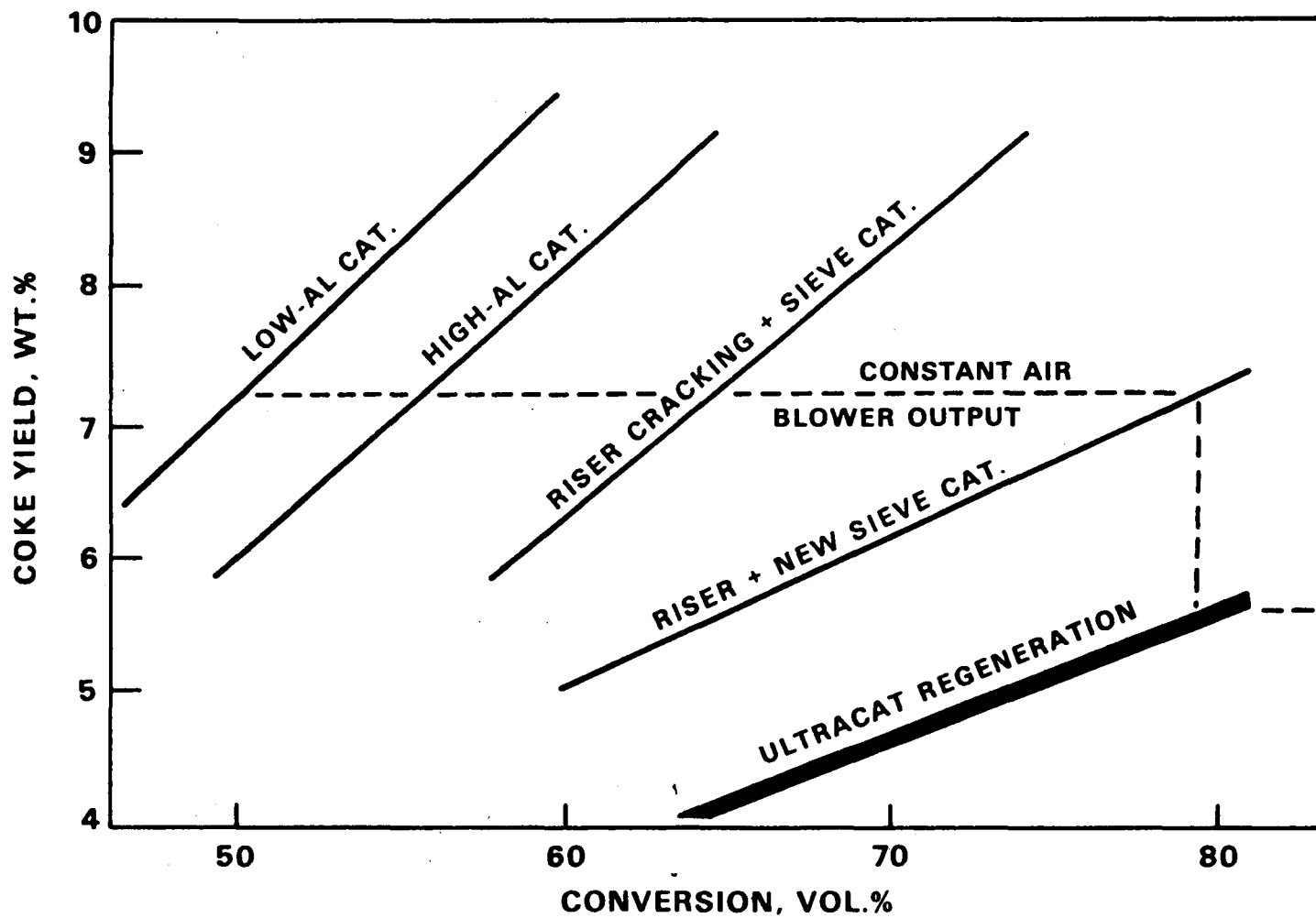


FIGURE VI-1 EVOLUTION OF FLUID CRACKING (UNIT C*, 1947-73)

*With constant air-blower output.

Source: Standard Oil Co. (Ind.)

A fundamental question regarding these modifications is whether they constitute a major reconstruction as defined in the FR,²⁵ since reconstructed facilities must comply with NSPS regardless of the emission change. Clearly, the modification standard does not apply, since the emissions from the HTR conversion units are equal to or less than those from the pre-conversion case.

Part 60 of the regulations specifies that reconstruction occurs upon replacement of components if the fixed capital cost of the new components exceeds 50 percent of the fixed capital cost required to construct a comparable new facility. By definition, "facilities" are identifiable pieces of process equipment or individual components which, when taken together, comprise a source. A strict interpretation of the regulation would mean that modifications to an FCC regenerator which cost more than 50 percent of a new regenerator would classify as reconstructed facilities and have to meet NSPS. Depending on the cost, this potentially includes revamping for HTR.

Clearly, the cost of modifying the regenerator for HTR relative to the cost of a new regenerator is an important relationship to evaluate. Rough estimates of the HTR conversion costs versus new facilities costs are shown in Table VI-1.

The conversion cost for HTR is based upon costs associated with a recent conversion at Exxon Company, U.S.A. The catalyst regenerator and air blower represents roughly 40% of the investment for a new FCC unit. Based on this example, the cost of revamping for HTR is about 15% of the cost of a new regenerator. If the revamping costs were understated by a factor of 2, it still represents only 30% of the new facility. Hence, FCC equipment modifications for HTR will not generally classify as reconstructed sources, and NSPS will not apply.

In Chapter V, it was noted that some of the projected capacity expansions will be achieved by HTR conversions. However, there is no data to determine what fraction of the capacity additions will be a result of HTR. Since the total growth in capacity is relatively small (<1% per year through 1985), we assumed for the NSPS impact evaluation that all this capacity would have to meet new performance standards. This slightly overstates the impact of NSPS, so that the results represent a maximum case. The alternative is to make a gross estimate of the capacity increase due to HTR, which is an exercise in hair splitting, since the total contribution is not very significant.

TABLE VI-1

ESTIMATED COST OF FCC REGENERATOR
MODIFICATIONS AND NEW EQUIPMENT

Capacity - 45,000 Bbl/Day

	<u>New</u>	<u>Modified</u>
Capital Investment ¹ (1975)		\$10 ⁶
New FCC Unit	21.6	--
Regenerator	8.6	1.2
Modified - Percent of New	--	14

¹ Materials and Labor

Source: Hydrocarbon Processing, 1974 Refining Handbook, and
Exxon R&E.

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APPENDIX A

SUMMARY OF EMISSION DATA

The available emission data on uncontrolled and controlled fluid catalytic cracker regenerators are presented in this appendix. The uncontrolled emission data are split into two categories according to principal pollutants. The first category contains emission data and test results for CO, SO_x, and NO_x including the following:

- a) V. H. Sussman Data (1957)
- b) Summary of test data from EPA National Point Source Data Bank
- c) Source Sampling Results on selected FCC units in SOCAL and ARCO refineries.

In the second category are emission data which report hydrocarbons as well as other constituents. Included in this category are:

- a) V. H. Sussman Data (1957)
- b) Emission ranges reported in Ctvrtnicek, etal., "Refinery Catalytic Cracker Regenerator SO_x Control Process Survey"
- c) Typical uncontrolled FCC emissions presented in Exxon scrubber technical sales literature.

Finally, typical emissions from the Exxon jet scrubber system applied to a FCC unit are presented.

Neither Standard of Indiana nor Exxon Company would provide hard data on SO_x or hydrocarbon emissions based on FCC stack sampling tests. ADL has informed both companies that EPA may request permission to perform on-site tests to determine hydrocarbon emissions from UltraCat regenerator (Amoco) and SO_x/particulate emissions from the jet scrubber (Exxon).

A sample calculation for estimating FCC regenerator flue gas volume is also provided in this appendix.

1. SO_x/NO_x/CO

TABLE A-1

EMISSIONS OF SULFUR OXIDES, AMMONIA, AND CYANIDES FROM STACKS OF FLUID AND THERMOFOR CATALYTIC CRACKING UNITS^a (Sussman, 1957)

Type	SO ₃ lb/hr	SO ₂			Totals as SO ₂ , vol %	Wt % SO ₃ in total oxides of sulfur	NH ₃		Cyanides as HCN		
		Chemical anal.		MS, ^b ppm			lb/hr	ppm	Chemical anal.		MS, ^b ppm
		lb/hr	ppm						lb/hr	ppm	
FCC	164	535	438	47	0.055	23.5	130	401	0.250	0.48	430
FCC	12.0	362	512	220	0.540	3.2	27.0	140	0.280	0.94	360
FCC	1.20	1,260	2,190	1,850	0.220	0.1	20.5	134	Trace	Trace	240
FCC	8.90	453	308	20	0.031	1.8	26.0	67	0.291	0.47	170
TCC	1.25	17.5	114	-	0.011	6.7	1.20	29	0.010	0.15	-
TCC	-	-	-	-	-	-	-	-	-	-	-
FCC	6.90	648	984	-	0.098	1.1	118	675	0.054	0.19	-
TCC	5.10	15.1	86	15	0.011	25.0	4.60	99	0.005	0.07	370
TCC	2.0	14.0	65	10	0.008	13.0	3.40	60	0.060	0.70	230
TCC	1.60	18.7	151	-	0.016	7.9	2.20	67	Trace	Trace	-
TCC	2.70	13.2	136	91	0.016	17.0	1.90	74	Trace	Trace	90
TCC	5.74	13.0	105	-	0.015	30.6	1.56	47	Trace	Trace	-
TCC	7.77	11.1	97	60	0.015	41.2	3.12	103	Trace	Trace	180
FCC	3.07	205	1,310	360	0.130	1.4	23.0	550	0.018	0.27	190
TCC	0.62	24.4	141	15	0.014	2.5	2.80	61	0.039	0.54	220

^aAll concentrations are reported on a dry basis.

^bMS = mass spectrophotometer.

TABLE A-2

EMISSIONS OF ALDEHYDES, OXIDES OF NITROGEN, CO₂, O₂, CO, AND N₂ FROM STACKS OF FLUID AND THERMOFOR CATALYTIC CRACKING UNITS^a (Sussman, 1957)

Type	Aldehydes as HCHO,		NO _x as NO ₂ ,		NO by MS, ppm	CO ₂ , vol %,		O ₂ , vol %,		CO, vol %, ORSAT	N ₂ , vol % by diff, ORSAT
	lb/hr	ppm	lb/hr	ppm		ORSAT	MS	ORSAT	MS		
FCC	77.0	130	26.0	29	250	8.7	11.1	5.1	2.2	4.9	81.0
FCC	18.0	53	4.2	8	-	8.5	8.8	3.5	4.1	7.8	80.2
FCC	25.9	96	163	394	160	10.0	11.8	2.3	2.3	6.1	81.6
FCC	4.0	5	202	191	11	13.4	13.4	2.0	2.3	0	84.6
TCC	3.5	49	5.7	51	-	8.2	-	7.9	-	1.4	82.5
TCC	-	-	-	-	-	-	-	-	-	-	-
FCC	0.9	3	5.9	12	-	9.5	-	2.7	-	6.8	81.0
TCC	2.2	26	0	0	200	9.2	12.1	6.6	-	3.2	81.0
TCC	1.2	12	0	0	170	4.7	9.0	13.5	-	0.7	81.1
TCC	0.6	12	3.1	34	-	9.6	-	8.3	-	1.5	80.6
TCC	0.4	9	2.2	32	190	12.8	13.3	2.5	2.5	3.6	81.1
TCC	2.6	44	2.7	30	-	8.4	-	9.8	-	0	81.6
TCC	3.4	63	0.6	7	130	8.8	9.2	7.8	11.1	2.6	80.8
FCC	1.5	20	-	-	310	7.8	7.8	5.1	5.5	6.1	81.0
TCC	14.3	177	7.7	62	230	9.0	9.0	6.9	7.3	4.1	80.0

^aAll concentrations are reported on a dry basis.

Source: Danielson, J. A., Air Pollution Engineering Manual.

TABLE A-3

TEST DATA FROM EPA DATA BANK

<u>Company</u>	<u>Location</u>	<u>Approximate Capacity (Bbl/day)</u>	<u>tons/year</u>					<u>CO Boiler or Afterburner</u>
			<u>Part.</u>	<u>SO_x</u>	<u>NO_x</u>	<u>HC</u>	<u>CO</u>	
Mobil	Los Angeles	50,000	33	4,450	2,450	0	0	Yes
SoCal	El Segundo	70,000	100	5,700	--	--	--	Yes
Getty	Philadelphia	50,000	15,300 ¹	61,300	--	--	--	Yes
Rock Island Refinery	Indianapolis	15,000	67	476	89	105	33,700	No
Ashland	Kentucky	60,000	1,550	959	--	--	6,020 ²	Yes
Cities Service	Lake Charles, La.	?	--	3,110	--	3	788	?
Exxon	Louisiana	?	--	92	33	--	58,000	Yes
Cont. Oil	Montana	16,000	110	898	--	--	58,700	No
?	Montana	9,000	--	3,270	--	--	--	No
Exxon	Montana	30,000	251	--	--	--	--	Yes
Texaco	New Jersey	40,000	500	530	410	0	0	No
Exxon	New Jersey	130,000	2,090	--	--	--	--	Yes
Sun Oil	Ohio	53,000	45	--	--	--	--	No
Sun Oil	Ohio	70,000	59	--	--	--	--	No
Texaco	Tulsa	31,000	3	--	--	--	--	No
Gulf	Philadelphia	20,000	63	283	0	--	--	No
Gulf	Philadelphia	52,000	1,140	2,750	0	--	0	No
Chevron	Utah	6,000	219	500	--	--	--	Yes
Amoco	Utah	153,000	176	2,670	--	--	--	Yes

¹No elect. precipitator or cyclone.

²Corresponds to 99.8% control efficiency.

RESEARCH REPORT

on

SOURCE SAMPLING OF FLUID CATALYTIC CRACKING
PLANT (ELECTROSTATIC PRECIPITATORS AND CO
BOILER) OF STANDARD OIL OF CALIFORNIA,
RICHMOND, CALIFORNIA

Contract No. 68-02-0230

Task Order No. 3

EPA Report No. 71-PC-20

to

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR PROGRAMS

July 6, 1972

by

E. J. Schulz, L. J. Hillenbrand,
and R. B. Engdahl

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

TABLE A-4

GAS COMPOSITION*

Standard Oil of California

Run No.	Date	Time	Moisture, Percent (a)	CO ₂ , Percent (b)	O ₂ , Percent (b)	NO _x , ppm (c)	O ₂ , Percent (d)	CO, ppm (e)	N ₂ , Percent (f)
1	12-16-71	1:20 pm		13.0	4.0		4.0	14	83.0
			17.9			104	3.7	14	
		2:40 pm		14.0	3.5		4.5	14	82.5
2	12-17-71	10:50 am		14.0	4.0		---	0.5	82.0
			19.4			100	---	0.5	
		12:00 pm		14.0	4.0		4.0	0.5	82.0
3	12-17-71	2:10 pm		14.0	4.0		4.0	0.5	82.0
			19.7			116	4.0	0.5	
		4:00 pm		14.0	4.0		4.0	0.5	82.0

(a) EPA particulate train method (Federal Register, Vol. 36, Part II, No. 159 (August 17, 1971).

(b) Fyrite (grab sample).

(c) Evacuated flask, EPA (grab sample).

(d) Beckman Model 715 (continuous sample).

(e) Beckman Model 215A (continuous sample).

(f) Calculated by difference.

* downstream of ESP and CO boiler

SOURCE TESTING--EPA TASK NO. 8

STANDARD OIL COMPANY
Richmond, California

by

E. P. Shea

Midwest Research Institute
Kansas City, Missouri 64110

EPA Contract No. 68-02-0228
(MRI Project No. 3585-C)

TABLE A-5

SUMMARY OF STACK GAS RESULTS^b

RUN	DATE	CO ^{a/}	NOX AS NO2		SO2	
		----- (PPM-DRY)	----- (LB/DSCF)	----- (PPM-DRY)	----- (LB/DSCF)	----- (PPM-DRY)
1	2-08-72	10.0	.0000143	120	.0000483	292
			.0000160	135		
			.0000121	101		
			.0000137	116		
2	2-09-72	9.0	.0000149	125	.0000658	397
			.0000156	131		
			.0000174	146		
			.0000184	155		
3	2-10-72	11.0	.0000182	153	.0000681	411
			.0000157	132		
			.0000176	148		
			.0000189	159		

^{a/} Determined with NDIR instrument and corrected for CO₂ interference.

^{b/} downstream of CO boiler.

SOURCE TESTING
EPA TASK NO. 6

STANDARD OIL OF CALIFORNIA COMPANY
El Segundo, California

by

Chatten Cowherd

Midwest Research Institute
Kansas City, Missouri 64110

EPA Contract No. 68-02-0228
(MRI Project No. 3585-C)

TABLE A-6

SUMMARY OF RESULTS (STACK GAS COMPOSITION)^{a/}

<u>Run</u>	<u>Date</u>	<u>CO^{b/}</u> <u>(ppm/vol)</u>	<u>NO_x as NO₂</u>		<u>SO₂</u>	
			<u>(lb/dscf)</u>	<u>(ppm, dry)</u>	<u>(lb/dscf)</u>	<u>(ppm, dry)</u>
1	12/14/71	-	1.31 x 10 ⁻⁵	108	-	-
2	12/15/71	-	1.39 x 10 ⁻⁵	114	2.23 x 10 ⁻⁵	132
			1.47 x 10 ⁻⁵	121		
			1.24 x 10 ⁻⁵	102		
			1.46 x 10 ⁻⁵	120		
3	12/16/71	-	1.72 x 10 ⁻⁵	142	5.48 x 10 ⁻⁵	324
			1.97 x 10 ⁻⁵	162		
			1.67 x 10 ⁻⁵	138		
4	12/16/71	5	1.75 x 10 ⁻⁵	144	6.09 x 10 ⁻⁵	360
			1.64 x 10 ⁻⁵	135		

a/ Excluding Orsat analysis. -- downstream of CO boiler.

b/ Determined with NDIR instrument and corrected for CO₂ interference.

SOURCE TESTING--EPA TASK NO. 6

ATLANTIC RICHFIELD COMPANY
Wilmington, California

by

E. P. Shea

Midwest Research Institute
Kansas City, Missouri 64110

EPA Contract No. 68-02-0228
(MRI Project No. 3585-C)

TABLE A-7

SUMMARY OF RESULTS (STACK GAS POLLUTANTS)^b

<u>Run</u>	<u>Date</u>	<u>CO_a</u>	<u>NO_x as NO₂</u>		<u>SO₂</u>	
		(ppm. dry)	(lb/dscf)	(ppm. dry)	(lb/dscf)	(ppm. dry)
1E	1/11/72	35	1.87 x 10 ⁻⁵	157	--	--
			2.04 x 10 ⁻⁵	172		
1W	1/11/72	6	2.00 x 10 ⁻⁵	168	--	--
			2.04 x 10 ⁻⁵	172		
			2.33 x 10 ⁻⁵	196		
			1.91 x 10 ⁻⁵	160		
2E	1/12/72	12	2.09 x 10 ⁻⁵	176	5.26 x 10 ⁻⁵	318
			1.90 x 10 ⁻⁵	160		
			1.97 x 10 ⁻⁵	165		
			1.80 x 10 ⁻⁵	151		
2W	1/12/72	12	1.14 x 10 ⁻⁵	96	4.75 x 10 ⁻⁵	287
			1.52 x 10 ⁻⁵	128		
			1.51 x 10 ⁻⁵	127		
			1.61 x 10 ⁻⁵	135		
3E	1/13/72	12	1.92 x 10 ⁻⁵	162	5.50 x 10 ⁻⁵	332
			2.02 x 10 ⁻⁵	170		
			2.78 x 10 ⁻⁵	233		
			2.40 x 10 ⁻⁵	202		
3W	1/13/72	37	1.78 x 10 ⁻⁵	150	7.08 x 10 ⁻⁵	428
			2.00 x 10 ⁻⁵	168		
			2.17 x 10 ⁻⁵	183		

a/ Determined with NDIR instrument and corrected for CO₂ interference.

b/ downstream of CO boiler.

RESEARCH REPORT

on

SOURCE SAMPLING OF FLUID CATALYTIC CRACKING, CO
BOILER, AND ELECTROSTATIC PRECIPITATORS AT THE
ATLANTIC RICHLFIELD COMPANY, HOUSTON, TEXAS

Contract No. 68-02-0230

Task Order No. 3

EPA Report No. 71-PC-19

to

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR PROGRAMS

July 6, 1972

by

E. J. Schulz, L. J. Hillenbrand,
and R. B. Engdahl

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

TABLE A-8

GAS COMPOSITION*Plant Atlantic Richfield Company

Ln o.	Date	Time	Percent Moisture (a)	Percent CO ₂ (b)	Percent O ₂ (b)	NO _x ppm (c)	Percent O ₂ (d)	CO ppm (e)	Percent N ₂ (f)
1	12/8/71	4:50 pm		13.0	4.0		4	0	83
			13.9				(g)	(g)	
		6:00 pm		13.0	4.0	78	(g)	(g)	83
2	12/9/71	11:55 am		13.0	3.0		3	0	84
		12:30 pm	14.5	14.0	2.0	76	2.2	0	
		2:40 pm		13.0	3.0		3	0	84
3	12/9/71	4:00 pm		12.0	3.8		3.8	0	84.2
			17.5				3.8	0	
		5:35 pm		12.0	3.8	89	3.8	0	84.2
4	12/10/71	11:30 am		14.0	3.0		3.0	0	83
			16.5				3.0	0	
		1:10 pm		14.0	3.0	70	3.0	0	83

a) EPA particulate train method (Federal Register, December 23, 1971, Vol. 36, Part II, No. 247).

b) Fyrite (grab sample).

c) Evacuated flask, EPA (grab sample).

d) Beckman Model 715 (continuous sample).

e) Beckman Model 215A (continuous sample).

f) Calculated by difference.

g) Rain water in sample train.

* downstream of CO boiler.

2. Hydrocarbons, etc.

TABLE A-9

TOTAL HYDROCARBON EMISSIONS FROM FLUID AND THERMOFOR CATALYTIC
CRACKING UNIT STACKS^a (Sussman, 1957)

Type	Mass spectrometer				Infrared spectrophotometer	
	Hydrocarbons	Hydrocarbons	Wt % C ₁ and C ₂	Vol % C ₁ and C ₂	Hydrocarbons (as hexane), tons/day	Hydrocarbons (as hexane), ppm
FCC	7.4	1,213	67.7	87.4	2.80	142
FCC	3.1	1,150	84.1	94.6	0.89	78
FCC	2.1	760	68.3	85.5	0.60	65
FCC ^c	1	98	42.3	54.1	0.30	12
TCC ^e	-	-	-	-	0.02	8
TCC ^e	-	-	-	-	0.02 ^h	-
FCC ^{d, e}	-	-	-	-	1.20	116
TCC ^d	0.4	308	40.9	70.8	0.04	13
TCC ^d	0.5	4,484	55.1	81.4	0.14	43
TCC ^{b, c}					g	-
TCC ^{b, c}	0.1	87	79.5	77	0.02	14
TCC	0.5	121	67.4	67.8	f	-
TCC					0.02	9
FCC	0.3	328	51.2	75.3	-	Trace
TCC	1.4	1,655	61.9	18.8	0.30	108

^aAll concentrations are reported on a dry basis.

^bOnly the mass spectrometer results for Units F-2T and F-4T were reliable. Since Units F-1T and F-2T and Units F-3T and F-4T are twin units, the data shown result from combining the twin units.

^cNo methane present as determined by mass spectrometer.

^dMass spectrometer determinations include oxygenated C₄ and C₅ hydrocarbons.

^eThe mass spectrometer results were not reliable.

^fThe infrared spectrophotometer results were not reliable.

^gConcentrations of hydrocarbons are below limit of accuracy of the infrared spectrophotometer.

^hInfrared spectrophotometric determinations were made on Unit D-1T only. The results shown were obtained by assuming that twin Unit D-1T and D-2T emit the same quantity of hydrocarbons.

Source: Danielson, J. D., Air Pollution Engineering Manual.

TABLE A-10

EMISSION RANGES FROM FLUID CATALYTIC CRACKING UNIT
REGENERATOR, BEFORE AND AFTER CO BOILER

Fresh Feed Rate, bpsd 156,000

Recycle Feed Rate, bpsd 35,000

	<u>Before CO Boiler</u>	<u>After CO Boiler*</u>
Stack Discharge Rate, scfm (60°F, 1 atm, dry basis)	484,000	Up to 30% Volume Increase (On Wet Basis)
Temperature, °F	1000-1200	485-820
Emissions:		
Sulfur Dioxide, ppm**	140-3300	Up to 2700 [†]
Nitrogen Oxides (as NO ₂) ppm	8-394	Up to 500 [†]
Carbon Monoxide, % vol.	7.2-12.0	0-14 ppm
Carbon Dioxide, % vol.	10.5-11.3	11.2-14.0
Oxygen, % vol.	0.2-2.4	2.0-6.4
Moisture, % vol.	13.9 - 26.3	13.4-23.9
Nitrogen, % vol.	78.5-80.3	82.0-84.2
Hydrocarbons, ppm	98-1213 ^{††}	-
Ammonia, ppm	0-675	-
Aldehydes, ppm	3-130	-
Cyanides, ppm	0.19-0.94	-
Particulates, grains/scf	0.08-1.39	0.017-1.03

* Emissions after CO boiler will be affected by the type of supplemental fuel and operating conditions in the CO boiler

** It was reported that up to 60% of sulfur oxides in regenerator flue gas may appear as SO₃ (see page 85)

† Estimated

†† Sussman Data

Source: Ctvrtnicek, et al, Monsanto
September 1974

TABLE A-11

Typical Uncontrolled FCCU Emissions Compared to
The Current Most Stringent Regulations

<u>Emission</u>	<u>Typical Data</u>		<u>Most Stringent Existing Source Regulations</u>	<u>Federal</u> (2)
	<u>Before CO Boiler</u>	<u>After CO Boiler</u>		
<u>Particulate (grains/DSCF)</u>				
Catalyst	0.2 - 0.6	0.1 - 0.4	0.0118	0.0388
<u>Opacity</u> , (Ringelmann No.)	← 1.0 to 3.0 →		1.0	1.5
<u>Gaseous Emissions</u>				
SO _x (vppm)	← 200 to 700 →		150-200 ⁽¹⁾	(3)
CO (vol.%)	10	< 0.1	0.02	0.05
NH ₃ (vppm)	200	< 10	*	*
HCN (vppm)	< 200	< 10	*	*
NO _x (vppm)	< 10	100-200	*	*
Hydrocarbon (vppm)	< 500	< 10	*	*

Note:

* Unregulated in a FCC at present.

(1) Normally set by ground level concentration. Several states have source standards applicable to FCC units.

(2) Federal regulations pertain only to new emission sources. States are allowed to set standards for existing FCCU's and they need not be equal to or more stringent than the federal regulations.

(3) Set by ground level concentration, must be calculated for each location. EPA has solicited bids for conducting research in area of FCCU SO_x emissions reduction as a step in setting standards.

Source: Exxon Engineering - Petroleum Department.

3. Jet Scrubber Emissions

TABLE A-12
EXXON JET SCRUBBER
Pilot Plant Performance Data
FCCU Stack Gas Scrubbing

<u>Range of Pollutant Loadings to Scrubbers</u>	<u>Performance (Collection Efficiency) of Scrubbers on Pollutants</u>
SO_x^* 200-500 vppm	SO_x 95-99%
<u>Particulate</u> - <u>Catalyst</u> 0.1-0.3 grains/SCF - <u>Condensables**</u> 0.1-0.2 grains/SCF	<u>Particulate</u> - <u>Catalyst</u> 85-95% - <u>Condensables**</u> up to 90%

Notes:

* Typical SO_x concentration is about 300 vppm.

** Sulfates and traces of hydrocarbons collected by wet test method.

Source: Exxon Engineering - Petroleum Department.

TABLE A-13

SAMPLE CALCULATION OF GAS
VOLUME FOR FCC REGENERATORS

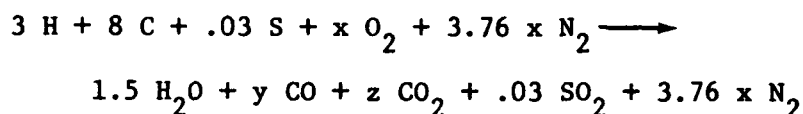
Note: This calculation is for the case of a gas stream from a traditional-type regenerator upstream of a CO boiler.

Assume coke composition is 96% C, 3% H, 1% S.

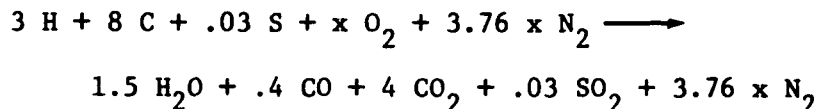
For 100 lbs coke, there are: $\frac{96}{12} = 8$ moles C

$$\frac{3}{1} = 3 \text{ moles H}$$

$$\frac{1}{32} = .03 \text{ moles S}$$



Assume that the ratio CO_2/CO is 1.0 (typical value).
Then, $y = z = 4.0$. Thus, the equation can be rewritten:



To satisfy the oxygen requirement of the right-hand side of this equation,

$$x = \frac{1.5}{2} + \frac{.4}{2} + 4 + .03$$

$$= 6.78$$

Therefore, the total moles of gas per 100 lbs. coke is:

$$1.5 + .4 + 4 + .03 + (3.76)(6.78) = 35.02 \text{ moles}$$

Assume the coke yield by traditional regeneration is 6.0% by wt. of fresh feed. Then, the weight of coke per barrel is as follows:

$$(1 \text{ bbl})(0.9 \text{ sp. gr.})(8.33 \text{ lbs/gal})(42 \text{ gal/bbl})(.06) = 18.89 \text{ lbs coke/bbl}$$

For a catalytic cracking unit processing 50,000 bbl/day:

$$\text{Gas volume} = (35.02 \text{ moles/100 lbs coke})(379 \text{ scf/mole})(18.89 \text{ lbs coke/bbl})$$

$$\frac{(50,000 \text{ bbl/day})}{(24)(60)} = 87,055 \text{ scfm}$$

APPENDIX B

LIST OF CONTACTS

In this Appendix are listed the names, addresses, and telephone numbers of individuals contacted for information in the course of this study,

VENDORS

Richard C. Herout
Coordinator, Environmental Engineering
Universal Oil Products Company
Process Division
20 UOP Plaza
Des Plaines, Illinois 60016
(312) 391-2880

Jim Montgomery
Davison Chemical Company
Division of W. R. Grace
10 E. Baltimore Street
Baltimore, Maryland 21202
(301) 727-3900

Albert Chatard
Davison Chemical Company
Division of W. R. Grace
10 E. Baltimore Street
Baltimore, Maryland 21202
(301) 727-3900

Chris Earl
Davy Power Gas
Drawer 5000
Lakeland, Florida 33801
(813) 646-7100

STATE AND LOCAL CONTROL AGENCIES

Illinois - Dr. John Reed
Supervisor of Permit Review Unit
Illinois Environmental Protection Agency
2200 Churchill Road
Springfield, Illinois 62706
(217) 782-5562

Indiana - Edward Stresino
Chief of Enforcement
Indiana Environmental Management Board
1330 W. Michigan
Indianapolis, Indiana 46206
(317) 633-4273

STATE AND LOCAL CONTROL AGENCIES Continued

Kansas - Robert Wallace
Kansas Country Control Board
Kansas City, Kansas
(913) 321-4803

Louisiana - Orey Tanner
Administrator, Technical Assistance Unit
Louisiana Air Control Commission
P. O. Box 60630
New Orleans, Louisiana 70130
(504) 527-5119

New Jersey - Tom Leonard
Department of Environmental Protection
Division of Air Pollution
P. O. Box 1390
Trenton, New Jersey 08625
(609) 292-6724

Ohio - Howard Johnson
Engineer
Ohio Environmental Protection Agency
361 E. Broad Street
Columbus, Ohio 43216
(614) 466-6116

Oklahoma - John Drake
Air Quality Division
Oklahoma State Department of Health
3400 N. Eastern Avenue
Oklahoma City, Oklahoma 73105
(405) 271-5220

Pennsylvania- Frank Willard
Air Pollution and Noise Control
Pennsylvania Department of Environmental Resources
Norristown Regional Office
Norristown, Pennsylvania
(215) 631-2415

Texas - Dr. Frank Spuhler
Regulations Applications
Texas Air Control Board
1100 W. 49th Street
Austin, Texas 78756
(512) 451-5711

STATE AND LOCAL CONTROL AGENCIES Continued

Washington - Michael Landor
Air Quality Division
Washington Department of Ecology
P. O. Box 829
Olympia, Washington 98504
(206) 753-2800

OPERATING COMPANIES

Mr. R. C. Mallatt
Manager, Environmental and Energy Conservation
Standard Oil of Indiana
200 E. Randolph Drive
Chicago, Illinois 60601
(312) 856-5485

Charles T. Rau
Environmental Control and Safety Division
Exxon Research and Engineering Company
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Florham Park, New Jersey 07932

Terry Day
Exxon Research and Engineering Company
P. O. Box 101
Florham Park, New Jersey 07932
(201) 474-6206

APPENDIX C

REPORTS AND CORRESPONDENCE

This appendix contains copies of written responses to our inquiries, trip reports, and summaries of telephone calls made in connection with this study.

1. Visits

As part of this study, ADL staff members visited with three companies, Standard Oil of Indiana (AMOCO), Exxon Research and Development Company, and Universal Oil Products Company. The results of our discussions are incorporated into this report. Summaries of the meetings are presented here. In each case a list of questions was forwarded to the company prior to our visit.

a. AMOCO

REVISED NOTES OF MEETING BETWEEN A.D. LITTLE AND AMOCO OIL ON FLUID CATALYTIC CRACKING

The following notes provide the revised answers on the specific questions.

1) Will HTR be universally adopted?

Amoco feels that, in the near future, 1/3 of all FCC units will be equipped for HTR. In the longer term, 1/2 will have this capability. This will be reached mostly through revamps of existing equipment. Of new units, the vast majority will be equipped for HTR. Amoco has converted 5 of its 11 units and has plans for additional conversions. UltraCat technology has been licensed for use in four additional units. In making the decision whether or not to revamp, the economics for each specific case must be considered.

2) How much excess air is required for HTR?

It depends on the catalyst and the regenerator design. A range of 3-25% excess air has been observed--for UltraCat, typically 5%. When a CO promoter is used, more excess air is required.

No changes in air blower capacity are needed since the reduced coke-make by HTR (better catalyst selectivity) cancels the additional air requirement per pound of carbon. Air distribution becomes a critical factor, however.

3) Under what conditions is a CO combustion promoter catalyst used?

Promoter catalysts reduce the dilute phase temperature, and can thus be used where metallurgy is an important consideration. There are yield penalties associated with promoter catalysts, however, due to the higher amount of carbon on catalyst. In other words, regeneration

with the promoter catalyst is not as effective as using a high temperature, so catalyst selectivity suffers. Amoco sees no unique benefits for these catalysts and has phased them out of its refineries. Experimentation is continuing on a smaller scale, however.

- 4) What is the mechanism by which promoter catalysts work?

The promoter increases the rate of oxidation of CO without directly affecting the yield structure on the reactor side. Amoco has observed no adverse environmental effects, such as the formation of metal carbonyls.

- 5) How do hydrocarbon and NO_x emissions compare for HTR and CO boilers?

From an HTR unit, the NO_x is 5-20 ppm leaving the regenerator compared with >50 ppm leaving a CO boiler. The differential is mainly attributed to the higher flame temperature in the CO boiler. The nitrogen oxides for HTR appear to come from the air rather than from the nitrogen tied with coke.

Based on thermodynamic considerations, no significant amounts of residual hydrocarbons are expected to be present for the HTR. At high regenerator temperatures and with excess oxygen, the rate of oxidation of hydrocarbons being higher than the rate of CO combustion is expected to result in insignificant amounts of hydrocarbon emissions. A limited number of tests seems to confirm this. These tests have shown that typically the hydrocarbon emissions for HTR are in the range of 3 to 35 ppm.

COS and HCN have not been analyzed for in the regenerator stack. However, from chemical equilibrium considerations, no COS and HCN are anticipated when there is excess oxygen.

- 6) How difficult is it to revamp a unit for HTR and how expensive is it?

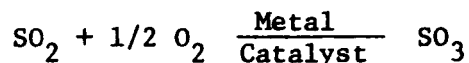
Most FCC units can be revamped, but the economics vary a great deal. Size is not the determining economic factor. Amoco feels that there is very little chance the revamp cost would exceed 50% of either the original or the replacement cost of the unit.

Amoco says that revamping for HTR does not necessarily increase the capacity of a unit. Whether the unit capacity increases or not depends on its operation prior to conversion to HTR.

- 7) What are typical values for SO_3/SO_2 ?

The Sussman data (1/125 to 1/1) were quoted, and Amoco said simply that their data fall within this range. In the 1971 NPRA Q&A session, it was pointed out that the ratio appears to depend on the metals on catalysts. Amoco does see this trend. It was pointed out that in

a few cases they have seen ratios above those expected for equilibrium for the reaction:



at the regenerator temperature. This is puzzling, and no theory was offered other than that the analytical techniques may be poor.

No increase in the ratio is observed when promoter catalysts are used.

- 8) If NSPS on SO_x were promulgated, would you meet it by hydrotreating the feed or by FGD?

Amoco believes that hydrotreating is not a viable option due to the high level of hydrotreating required. Even if a sulfur spec were placed on gasoline, Amoco would hydrotreat the gasoline fraction rather than the entire feed.

Either FGD or feed hydrotreating is expensive.

- 9) Are there any methods other than HTR and FGD for controlling SO_x ; e.g., steam stripping?

The Monsanto claims for steam stripping apply only to natural clay catalysts. One does not observe the substitution of water for adsorbed sulfur compounds on zeolites. Amoco further notes that the required steam stripping rates indicated by Monsanto are ten times higher than those typically used for FCC. This represents a great expense.

- 10) Is it possible that catalyst improvements will reduce SO_x ?

Amoco is carrying out proprietary work in this area.

- 11) Where do bottlenecks generally occur when a unit is expanded?

Amoco did not feel any generalizations were possible.

- 12) What are typical values for the equipment life and onstream factor?

FCC units are usually down for about one month every 3-4 years. This corresponds to an onstream factor of 97-98%. Equipment life varies considerably. Reactors and regenerators have lasted up to 30 years.

- 13) What are your projections for FCC expansions?

No projections are available. Amoco is looking at all ways of debottlenecking its own units.

Other General Comments

There was some discussion of the correlation between feed sulfur and coke sulfur. Two publications--one by Amoco and the other by Gulf--have addressed the issue; there was poor agreement between the two sets of data. Vasalos claims that the difference lies in the fact that Gulf used hydro-treated feeds for most of its data. If the points are taken for virgin stocks only, the two articles agree fairly closely. For unhydrotreated feedstocks, there appears to be a correlation between thiophenic sulfur and coke sulfur. Since thiophenic sulfur is difficult to remove by hydrotreating, severe hydrotreatment of feeds is necessary to reduce coke sulfur levels.

One would expect, generally, that SO_x emissions will go up as the FCC feed sulfur increases. As sour crudes are used increasingly, SO_x emissions will therefore increase.

b. Exxon Research and Engineering Company

EXXON'S RESPONSES TO ADL QUESTIONNAIRE

A. CHARACTERIZATION OF FCC REGENERATOR EMISSIONS

1. Q. Is there a correlation between FCC feed sulfur and catalyst coke sulfur content?
 - A. Studies by American Oil Co. indicate that the sulfur levels in coke are proportional to the feed sulfur level. Their findings indicate that the weight percent sulfur on coke produced from virgin feeds is about 0.7 of the weight percent sulfur in the feed. No definite correlation between fuel sulfur compound type and coke sulfur level has yet been determined. This is due to the large number of unanalyzed sulfur compounds in the feed.
2. Q. How do other operating variables such as cracking severity, recycle ratio, regenerator operation affect sulfur emissions?
 - A. Lowering of cracking severity and recycle ratios will result in a reduction in the quantity of SO_x emissions which is proportional to the reduction in total reactor coke. High temperature regeneration, however, reduces SO_x concentrations somewhat more than what would normally be observed for a given reduction in reactor coke make.

3. Q. What is the range of recycle ratios commonly used? NPRA (Blazek) stated that the nationwide average in the U.S. is 16% of F.F.
- A. Recycle ratios are dependent on the type of catalyst a refiner is using. Recycle ratios from 0 to 15 vol% on F.F. are common for operations utilizing a zeolitic catalyst. Operations with amorphous catalysts can be as high as 100 vol% on F.F. Recycle ratios will also vary seasonally as refiners gear up to produce either heating oil or gasoline products to meet consumer demands.
4. Q. What is a typical SO_3/SO_2 ratio for regenerator effluent?
- A. Typical SO_3/SO_2 ratios for CO boiler effluents, as operated by Exxon, are about 0.03 or less.
5. Q. If SO_x NSPS standards were promulgated, would you meet them via flue gas desulfurization (FGD) or feed hydrotreating (HT)?
- A. It is not possible to state generally which process, FGD or feed hydrotreating, is preferred in meeting SO_x standards. For a particular refinery the preferred system would be based primarily on economic considerations.
6. Q. Do you know of any means other than FGD or HT for SO_x control? For example, steam stripping?
- A. Presently, our only methods for SO_x control are by flue gas desulfurization and feed hydrotreating. However, we are aware that steam stripping is being investigated on a laboratory scale elsewhere.
7. Q. Could any catalyst improvements be made to reduce SO_x ? It is reported that silica-magnesia amorphous catalyst could reduce regenerator SO_x emissions. (NPRA-Blazek)
- A. We presently do not know of any catalyst or catalyst improvements that would result in the reduction of SO_x regenerator emissions.
8. Q. Will high temperature regeneration (HTR) be universally adopted?
- A. Exxon U.S.A. units do not operate under HTR for CO control since they all have existing CO boilers. However units are being converted to HTR due to the economic incentive of incremental yields.

9. Q. How much excess air is required for HTR to ensure essentially complete CO combustion?
- A. The quantity of excess air required to ensure complete CO combustion is dependent on catalyst types used. Combustion promoting catalysts require approximately 0.6 percent excess air, while ordinary zeolitic catalyst need approximately 1.5 percent excess air for complete CO combustion in HTR.
10. Q. Under what conditions are CO combustion promoter catalysts used?
- A. CO combustion promoting catalysts are generally used when it is not economical to use CO boilers or high temperature regeneration to meet desired CO levels in flue gases.
11. Q. What is the general mechanism by which the new catalysts work to promote CO oxidation? Are these catalysts essential for HTR?
- A. A possible mechanism by which the new catalysts works is that a finely dispersed layer of noble metals on the catalyst surface increases its ability to oxidize CO. These catalysts are not necessary for HTR operation.
12. Q. How do hydrocarbon and NO_x emissions from HTR compare with emissions with a CO boiler? Can you provide test results on emissions from FCCU?
- A. There is no significant difference in hydrocarbon emissions from HTR or a CO boiler. Concentrations of less than 10 vppm hydrocarbon have been observed in both types of operation in Exxon units. NO_x emissions from either configuration are lower than 200 vppm.
13. Q. How difficult is it, in general, to revamp a FCCU for HTR? How expensive is it?
- A. Revamping an FCCU for HTR operation involves the replacement of all carbon steel regenerator components with a more heat and erosion resistant material such as a type 304 stainless steel. Conversion to HTR can be accomplished in a normal turnaround. A recent conversion of a 45 kB/D unit to HTR as estimated to cost 1.8 M\$. This cost includes replacement of cyclones, plenum chamber, cyclone diplegs, regenerator grid and seals, and the catalyst overflow well.

14. Q. If FCCU expansion is necessary, where are the bottlenecks, and what is done to increase the unit's capacity? What effect do these changes have on emissions?
- A. In typical FCCU expansions, the major bottleneck areas are in the overhead gas compressors, solids separation systems, air blowers and feed preheat trains. Fresh feed capacity increases are sometimes obtained by using more active catalysts and more severe operating conditions to reduce the amount of recycle to the reactor. SO_x and CO emissions would be reduced if the regenerator were converted from low temperature regeneration to HTR in an expansion. Otherwise flue gas emissions will be proportional to coke make.
16. Q. What is the average equipment life for a FCCU? Average stream factor?
- A. The life of specific equipment components varies a great deal, however, the average economic life of a FCCU is 16 years. Average stream factors for domestic units are 96%.
17. Q. Are there any available projections of FCC capacity expansions? How would FCC feed desulfurization trends affect these projections, i.e., yield improvements?
- A. We do not have available any such projections.

EXXON SCRUBBER TECHNOLOGY

1. Q. Is there any literature on application of this control technology to FCC regeneration?
- A. The technology is available for licensing and the pertinent brochure is available.
2. Q. Has the control system been applied to FCCU? Where are these installations? How long have they been in operation on this source?

<u>A. LOCATION</u>	<u>SIZE (Design)</u> (ACFM)	<u>STARTUP DATE</u>
Baytown, Texas	300,000	March, 1974
Baytown, Texas	510,000	May, 1975
Baton Rouge, Louisiana	860,000	February, 1976
Bayway, New Jersey	590,000	May, 1976

3. Q. Were there any specific problems at the above locations? Upset conditions? Problems during start-up and shutdown? What was total time available to the FCC units since start-up?
- A. ● Overall performance has been good. There have been some metal loss problems in the scrubbing liquid delivery system due to erosion and corrosion.
- + The reasons for the problems have been identified and solutions are being implemented.
- Service factors on the two Baytown scrubbers (see answer to #2) have been 94 and 93% respectively since the beginning of 1975.
4. Q. What SO_x and particulate (if applicable) removal efficiency is attainable with the control system? Are there any supporting data available? Can we visit or phone contact the operating companies?
- A. ● Pilot plant operations have demonstrated the following:
- SO_x removal efficiencies of 90+%
 - Particulate collection efficiencies in excess of 85%
- Initial commercial operations have demonstrated the following:
- SO_x removal efficiencies in excess of 90%
 - Particulate collection efficiencies of up to 90%
- Testing of the Baytown scrubbers have confirmed that they have met all local control regulations and they also have met the Federal New Source Performance Standards for dry particulates.
- Supporting data has been made available through a licensing brochure and compliance data have been sent to local control authorities.
- Any follow-up should be handled through Exxon Research and Engineering Company.
5. Q. Are these problems related to oxidation and presence of SO_3 ? What is absorption capacity for NO_x ? Do installations have pre-scrubbers for removal of particulate matter?
- A. ● While there are no problems with SO_3 being present, it does, however, tie up part of the active component of the system's buffering agents.

- SO₃ levels are low and since the active portion of the buffer itself is subject to partial auto oxidation, no performance or operability debits occur.
 - To date the system has not been tested for NO_x removal capabilities. Such testing would only take place once all commercial systems have completed their shakedown phase.
 - The Exxon scrubbing system is capable of removing both particulates and sulfur oxides in a single operation. None of the Exxon Co. U.S.A. installations have particulate removal devices upstream of the scrubber.
 - The single step removal of both particulates and SO_x is a major processing advantage for our scrubber system.
6. Q. For new plants, what kind of guarantee would be extended? SO₂ removal efficiency? Outlet concentrations of SO₂ (ppm SO₂ on dry gas)? Operating factor? What are important operating conditions for the guarantees to apply? What is the time period for guarantees?
- A. ● Typically scrubber collection efficiencies are
- + Particulate -- 80+% collection efficiency
 - + SO_x -- 90+% collection efficiency
- However, in general, we are still firming up our guarantee package.
 - Many of the factors which would go into the guarantee package would be subject to specific negotiations for the particular location and application.
 - Our present thinking on the guarantee package is as follows:
 - We would guarantee the level of particulate and SO_x in the outlet gases from the scrubber for a specific design basis for the inlet gases and particulate to the scrubber at designed operating conditions.
 - However, depending on specific conditions an outlet "stopper" (vppm of SO_x) may be applied.
 - + Scrubber "service factor" is highly dependent on the owner's operating and servicing philosophy for the unit and is not usually covered by guarantees.
 - + Once our guarantees were met, we would normally consider this successful demonstration of the unit and allow no additional time factor.

7. Q. Control system experience in refinery applications. How many plants in the U.S.? Europe? Japan? Operating history? How does experience in Europe and Japan differ from U.S. practice?

- A.
- Exxon Co. U.S.A. currently has three (3) operating scrubbers and one (1) scheduled for startup within this quarter.
 - No units are currently operating or under construction outside of the U.S.A.
 - Capacity of the operating units is as follows:
 - 300 kACFM Baytown, Texas FCCU #2 Scrubber
 - 510 kACFM Baytown, Texas FCCU #3 Scrubber
 - 860 kACFM Baton Rouge, La. PLCA #2/PLCA #3 Scrubber
 - Slated for startup within this quarter is the Bayway, N.J. FCBW #2 scrubber with a capacity of 590 kACFM.
 - By mid 1976, 2260 kACFM of the flue gas will be treated by the Exxon scrubbing process.
 - Operating experience has been covered in response to question No. 3.

8. Q. What, in your opinion, are the major competing processes? What are the advantages and disadvantages of the competitive system?

- A.
- There are possibly two systems which are competitive with Exxon's Jet-Ejector venturi scrubber for both particulate and SO_x removal. These are:
 - Combined FCCU feed hydrodesulfurization (HDS) with ESP's
 - High energy venturi scrubbing
 - HDS/ESP's in general have the following advantages/disadvantages
 - Advantages
 - + FCCU yield credits through HDS
 - Disadvantages
 - + Operation of ESP sensitive to changes in FCCU operation
 - + Large onsite plot space requirements
 - High energy venturi scrubbing in general has the following advantages/disadvantages.
 - Advantages

- + Lower liquid circulation rate and consequently smaller circulating pumps.

- Disadvantages

- + Is only viable if "free" gas pressure drop is available at a suitable location such as downstream of a CO boiler.

- + If fans and/or blowers are required maintenance is increased.

- + Investment is greater than jet ejector scrubber when fans and/or blowers are used.

- In general, we have found the jet ejector wet gas scrubber to have the following advantages controlling both particulate and sulfur oxides:

- Control of several pollutants
- Operation is relatively insensitive to changes in FCCU operation.
- Excellent onsite plot utilization

- + Less duct work
- + Single unit
- + Offsite storage and disposal

- Technology will not readily become outdated.

- High service factor, low maintenance costs.

- Investment and operating costs are lower than comparable schemes for simultaneous control of particulates and sulfur oxides.

- Conclusions reached as to advantages/disadvantages apply in general. Specific refinery conditions such as environmental regulations; plot space; "grass-roots" or existing units; processing requirements; and other factors vary the choice of the optimum emission control system from refinery to refinery. Thus, the choice of system is highly dependent on the specific refinery.

9. Q. Do FCC units represent a significant market for air pollution control systems?

A. ● There are approximately 180 FCCU's in the USA

- Outside Exxon Co. USA we cannot speak with any authority on what percentage of units would require additional control measures.

- While there appears to be a potential market information as to the true potential must come from the operating companies.

ADL MEETING NOTES

EXXON R AND E--FLORHAM PARK, N.J.

Dr. Jashnani and Mr. Stickles of Arthur D. Little (ADL) attended a meeting at Exxon Research and Engineering (ER & E) in Florham Park on April 23, 1976. The meeting was held at the request of ADL to discuss air-borne emissions from FCCU and ER & E's control technology for FCC regenerator emissions. Representatives from Exxon R and E included:

John Cunic	- Project Engineer
Terry Day	- Senior Project Engineer
Charles Rau	- Project Engineer
Herbert Schroeder	- Technology Sales Engineer

Prior to the meeting, ADL had submitted a list of discussion questions against which ER & E had prepared written answers. A copy of ER & E's Q and A write-up is attached. The discussion of each Q and A during the meeting elicited other informative responses which are presented by question nos. below.

A. CHARACTERIZATION OF FCC REGENERATOR EMISSIONS

- Q-1 Copies of the referenced paper were provided by ER & E. ER & E are studying ways to predict coke sulfur from feed composition, but accurate modeling is difficult. Process design of FCCU is based upon operating experience and FCC mass balance data.

ER & E believe the trend is toward higher sulfur in feedstocks. Arabian Light seems to predominate as a marginal crude, however, Arabian Heavy should be considered as a study case. Typically, FCC feed from Arabian Light run 2-3% sulfur.

- Q-2 With conventional regeneration, sulfur emissions are directly proportional to coke make. For HTR, the incremental reduction in sulfur emissions is slightly better than 1 to 1 with reductions in coke make. The reason for this is not known, but it is observed.

Because HTR removes catalyst coke more effectively, the regenerated catalyst has a higher activity than with conventional regeneration. Hence, for a given yield structure, about 25 percent less coke is made. This means that feed or severity can be increased until the practical coke make limit is again reached. This potential for yield or capacity improvement is the major attractiveness of HTR.

The reduction of CO by HTR to 500 vppm has been demonstrated, however the temperature required ($\sim 1400^{\circ}\text{F}$) to achieve this CO level is not necessarily the economic optimum for yield improvement. ER & E believe there are temperature levels below that needed for compliance with CO regulations that give economic operation. At

these conditions CO boilers would still be needed to control CO emissions. In conclusion, the main incentive for HTR is yield improvement.

Catalyst addition with HTR may be slightly higher to maintain activity. However, catalyst attrition is nearly the same with HTR as practiced by Exxon USA.

Q-3 and 4 No significant additions to stated answers.

Q-5 There are no sweeping generalities, each situation has to be individually evaluated. In fact, ER & E look at both alternatives (CO-fining vs. scrubbers) when evaluating emission controls for FCCU. Naturally, plot space is an important factor in retrofit situations.

Q-6 Beside Monsanto's interest in steam stripping, ER & E is not aware of any other developments.

Q-7 Answer as stated.

Q-8 For new FCCU, ER & E believe some form of HTR would be applied, primarily to improve yields. Whether to go to CO control by this means would depend on the relative importance of steam (CO boiler economics) compared to the cost of HTR. HTR is the least capital intensive method of control; upgrading of metallurgy being the principal cost.

For existing FCCU with CO boilers, there is no incentive to go all the way to control CO by HTR. In this case, optimum conditions for yield gains would be selected.

Q-9 Exxon USA does not have any CO combustion promoting catalysts in operation.

Q-10 Promoter catalyst permit CO combustion to proceed at lower temperatures. This is of importance with existing FCCU where metallurgy limitations might not allow CO control by unpromoted HTR. However, to get yield improvements associated with HTR, high temperatures are essential. Consequently, promoter catalysts are used where CO control is the overriding consideration (short term solution). The ability to meet the CO limit at conventional regeneration temperatures will depend on the effectiveness of the promoter catalyst.

Q-11 Answer as stated.

Q-12 The concentration levels in both cases are after the CO boiler. Due to the difficulty of sampling upstream of the CO boiler, ER & E do not have a lot of test measurements on emissions leaving the regenerator. Reproducibility is also difficult due to the low

concentration of NO_x and hydrocarbons. Charles Rau will check on the availability of test data and determine if it can be released to ADL.

Q-13 and 14 In the past, FCC capacity was increased by 1) the use of improved zeolite catalysts and 2) increasing flow rate by raising operating pressure. HTR is the latest innovation for expanding FCC capacity. The reduction in coke make over conventional operation is utilized to increase capacity by running backup to the coke limit. Capacity can be increased by feed pretreatment, but this is usually not economical.

In general most operators have taken advantage of the expansion opportunities available through catalyst improvement and pressure operation. Immediate projects do not suggest that another round of expansions based on catalyst improvements is imminent.

The cost of conversion to HTR depends on the metallurgy of the existing unit. A typical cost is given in answer 13. ADL will find out what criteria are applied to define a new source and whether an increment in capital investment is included.

Q-15 FCC is a mature technology and the basic conversion, and, although design differences exist, yields and operating requirements are about the same for the licensed processes. For a given feedstock and operating condition, gaseous emissions should be basically similar. Particulate emissions will depend on cyclone design and the number of stages employed.

Q-16 ER & E see some evidence of a "new car fever" in FCCU expansion planning. Consideration is being given to new units, especially in cases where the existing unit is of World War II vintage. The ability to comply with local emission standards will be a factor affecting such decisions.

Q-17 ER & E suggested that ADL contact API, NPRA and the editorial staffs of O & GJ and Hydrocarbon Processing for projections on FCC capacity additions.

B. EXXON SCRUBBER TECHNOLOGY

Q-1 Answer as stated.

Q-2 The Baton Rouge scrubber handles gas from two FCC units.

Q-3 The problems were associated with the materials of construction. Better materials are now being specified.

Q-4 The ER & E scrubber system has been approved by the Texas Air Quality Board and can meet the state particulate and primary ambient air quality standards.

Q-5 No additions.

Q-6 No additions.

Q-7 Typical liquid to gas ratios for ejector scrubbers are 40-120 gpm/
1000 acfm.

Q-8 and 9 No additions.

As a final note, it was pointed out that the auxiliary fuel used in CO boilers can increase the sulfur concentration in the flue gas from FCC units.

C. UNIVERSAL OIL PRODUCTS COMPANY

UOP MEETING NOTES

April 29, 1976

Those present were:	Peter Stickles	- ADL
	Leigh Short	- UMass
	Hal Hammershaimb	- U.O.P.
	Dick Herout	- U.O.P.
	Dennis Michaelis	- U.O.P.
	Dick Conser (pt. time)	- U.O.P.

The meeting began with introductory remarks by Peter Stickles, outlining the objectives of the study, and emphasizing that no proprietary information was being sought. UOP commented that it was their understanding that this study would also not get into costs or technology under development. Aside from these areas they intend to cooperate fully but pointed out that since they are not an "operating" company they just do not have access to and cannot furnish some of the data questioned.

The numbers below refer to the question numbers as sent to U.O.P.

A1. There is no simple correlation between FCC feed sulfur and coke sulfur. A formerly widely used rule of thumb was that feed sulfur equals coke sulfur, but this "rule" is not too accurate. U.O.P. has done limited commercial testing for flue gas sulfur oxides--there has been no need for extensive commercial testing. Pilot plant data, while accurate in the analytical sense, must be used with care because these units are not always in heat balance. This may affect the sulfur balance. UOP agreed that the Gulf API paper of May 1975 was probably the most complete pilot plant information in the literature. UOP also emphasized that the quantity of sulfur in the coke is feed specific.

A2. The effect of other variables on sulfur emissions is hard to determine --very little commercial data is available. At high severity, if the sulfur compounds crack, the sulfur will end up as additional H_2S . Refractory sulfur compounds will tend to concentrate in the cycle oils. As recycle increases, it might be expected that more sulfur will show up on the coke. The residual sulfur on the coke after regeneration is very low.

A3. UOP plants in the U.S. probably average less than 16% recycle. New plants, using zeolite catalysts, can be designed for 5% or lower. Older plants may have originally been designed at 40% or even higher. A minimum recycle flow is generally used for return of entrained catalyst. The nationwide average will probably continue down. Recycle ratios are not much different for HTR operation --if anything the ratio is slightly less.

A4. Data is available indicating up to about 10% of the coke sulfur goes to SO_3 , but UOP pointed out that they have some questions about the analytical method used for SO_3 . (They used a modified version of the LA method rather than EPA's method.) U.O.P. knows of no data comparing SO_3 concentrations with varying regeneration techniques.

A5. There is no single, simple answer to this question. UOP stress that any standard-levels considered should be high enough so as to not take away control options that are viable and economic. If standards are developed (UOP questions their necessity and value at this time), they should be of such structure that several control options, including flue gas desulfurization and feed hydrotreating, are possible alternatives depending upon a refiner's specific considerations relating to such things as charge stock, product requirements, etc. Both primary alternatives will effectively reduce SO_x emissions and have distinct benefits. FGD may be less costly, depending on the process employed, but in the case of feed hydrotreating, it should be noted that there may be significant benefits in terms of increased yields, reduced gasoline and fuel oil sulfur levels and the potential for increased unit throughput. The choice for a particular case would depend on these considerations as well as individual economic factors, as discussed in UOP's 1974 NPRA paper.

A6. UOP is not aware of commercial employment of means other than flue gas desulfurization or feed hydrotreating for FCC SO_x control. They are aware of the Monsanto report which suggested steam stripping. Tho UOP does not have a concrete opinion on this, they believe that the industry feeling is that this would be a questionable method.

A7. Catalysts could probably be developed to reduce SO_x emissions to some extent, but U.O.P. does not specifically do this type of research. The catalyst manufacturers may have comments in this area.

A8. There is no single answer. HTR is not for everyone. These refineries who have CO boilers may not be able to justify HTR--in any event the CO boiler would likely be retained for some heat recovery. The refinery steam situation is important to this economic evaluation. For new cat cracker units, HTR with and without a CO boiler are possible options. Older units without CO boilers are considering revamping for HTR to comply with emission standards as well as to improve energy conservation. In addition to these factors, HTR has an advantage in improved activity of regenerated catalyst due to lower levels of residual carbon on regenerated catalyst. See UOP 1976 NPRA paper.

A9. The amount of excess air required depends upon operating conditions and design. Very little excess air is needed if the conditions are optimum. The typical range is 0-2% oxygen. With conventional regeneration, the range is 0.1-0.2% oxygen. U.O.P. has data on the effect of excess air on CO but not SO_x . Too much air may not be beneficial due to temperature and residence time considerations.

A10. CO promoter catalysts do not change the dense phase temperature, but do lower the peak temperature in the dilute phase. The catalysts cost more but can save money by requiring fewer metallurgical changes during a revamp, i.e., increases the degree of flexibility. There are no yield changes (using promoter

catalyst) per se. U.O.P. does see widespread use of these catalysts. For a light feedstock, requiring low regeneration temperatures, promoter catalysts are more likely to be used.

A11. The promoter catalysts are not essential for HTR operation.

A12. U.O.P. does not have data showing a comparison of HC/NO_x from HTR versus a CO boiler. Intuitively one would expect low levels of hydrocarbon in both cases since CO destruction is usually rate limiting, but lower NO_x for HTR (since no CO boiler). Metals are not present in significant quantity in the fines emitted to the atmosphere--cyclones remove 99% of the particulates, ESP almost all the rest.

A13. Each unit must be looked at individually. Often, for old units, the carbon steel in the regenerator, cyclones, slide valves, etc. will have to be replaced by 5 chrome or 18-8 stainless (which is better). The air blower is often the bottleneck.

ESP resistivity changes are not a problem with HTR if the gas is cooled to the "old" temperature--about 700°F.

Regarding costs, UOP pointed out that it is not reasonable to tie NSPS "Reconstruction" applicability for revamps to the cost of the regenerator alone. The way the regulations now read, what is actually a moderate revamp of an FCC would likely fall into the "Reconstruction" category of the regulations, which require a refiner to comply with the same stringent and costly standards as

new units. This could frighten some refiners away from otherwise justified revamps which would have reduced CO emissions and conserved energy.

A14. Expansions can be done in a number of ways. Alternatives or changes include:

- a) Zeolite catalysts (most FCC units now have this)
- b) Raise the pressure--this alters the entrainment of catalyst to the fractionator, but does increase capacity
- c) Desulfurize the feed--this can help if the process is air limited
- d) Install a parallel fractionator--some refineries have done this plus changed the air rate.

Refineries cannot tolerate high particulate emission rates, because of the expense of replacing the catalyst lost.

A15. ADL clarified the question by pointing out that they were not inquiring as to competitive differences or advantages between the processes, but rather whether they all would fall into the same emission category. In this context, UOP said that there are probably only minor differences in emissions from the several processes, but there are design differences.

A16. The operating factors are 95% (average 7 days/year downtime). Some FCC's have run continuously for six years, before maintenance turnarounds. SO_x standards would have to account for the long run times of FCC units versus the shorter times of FGD units.

A17. U.O.P. projects FCC operating capacity growth rate to 1985 of 0.5% per year (U.S. plus Canada). This reflects some change in lifestyle due to higher energy costs. If there is a severe adjustment in lifestyle--they project virtually no growth rate in FCC capacity to 1985. It is expected that in the U.S. 20,000 B/D is about the minimum size FCC unit that will be installed. U.O.P. projects an increase of roughly 150,000 B/D FCC capacity by 1980 above the 1974 capacity of approximately 5.2×10^6 B/D. This figure includes revamps. They had no information on how to split new versus replacement or revamp capacity increases. By comparison the FCC growth in the period 1966-74 was 2% per year.

FGD TECHNOLOGY

The following points were brought out by U.O.P.

1. SFGD capital costs should be less than VGO desulfurization (VGO also uses more hydrogen than SFGD, to achieve the same flue gas sulfur level.)
2. SO_2 removed (recovered) from the FCC will go to the Claus unit. Generally no major changes are expected here, as heat removal (steam generation) following H_2S oxidation is the usual thruput limitation on a Claus plant while SO_2 into a Claus may bypass this stage. The Claus plant should be checked in each case.
3. In establishing VGO-desulfurization severity, flue gas SO_x standards are not necessarily controlling. Product specifications on sulfur may establish the degree of sulfur removal in the VGO desulfurization unit.
4. There are no commercial Shell/UOP FGD units installed in the U.S. There is one in Japan processing flue gas from a residual fuel oil-fired boiler (40 MW).

5. UOP can provide no information on guarantees between JST (Japan-Shell Tech. Co.) and SYS (Showa Yokkaichi Sekiyu). UOP is prepared to guarantee flue gas capacity, percent desulfurization and acceptor life and perhaps other factors depending upon the specifics of a particular application. Guarantees can be fully discussed only in view of the specific technical and economic factors and financial liabilities.
6. The reactor internals of the SFGD reactor are designed to accept high loadings of entrained solids and can be located in the flue gas train without regard to solids removal equipment. The pilot operation at Tampa Electric has confirmed the above.
7. NO can be removed to any desired level. Removal to 100 ppm can be achieved at modest incremental cost increase over that for desulfurization. Performance data on the SYS unit are available.
8. It is considered that COS passes through the SFGD unit unreacted. This can be checked in the laboratory if necessary.
9. Above 90% sulfur removal, the SFGD costs starts to rise significantly. There is no specific technical limit.
10. Since the acceptance cycle of SFGD is an oxidation, it is necessary that the feed gases are in a completely oxidized condition and that a small amount of oxygen is present. SFGD could not be applied to flue gases from an uncontrolled FCC unit which may have 10% CO. However, FCCU flue gases from controlled units having complete CO combustion would have very low CO contents and would be satisfactory.

2. TELEPHONE CONVERSATION SUMMARIES

a. State and Local Air Pollution Control Regulations

In connection with this study we spoke with representatives of state and local air pollution control agencies of the states having a total FCC capacity of 100,000 BPSD. This represents 71% of total U.S. capacity, or 102 out of total 143 units. Questions asked related to two general areas:

1. Confirmation of regulations governing existing sources, and
2. Present utilization of CO boilers and trend in the next 10 years.

Listed below are the answers to these questions from all agencies contacted. Information appearing opposite number 3 is additional information received during conversation.

Illinois (John Reed)

1. Confirmed understanding of SO_x and hydrocarbon regulators.
2. 5 of the 9 refineries with FCC's have CO boilers, none recently installed. The trend seems to be more toward hot regeneration rather than use of CO boilers. Although HTR is still being studied, Reed thinks that 2 or 3 refineries presently having variances will move toward this process in the next few years.
3. Because of Illinois' low sulfur crude requirement, hydrotreating has not been popular in the state. Refineries are petitioning for a relaxation of this requirement, however, and if they win, hydrotreating might become more popular.

Many of the refineries have sulfur recovery plants.

Indiana (Ed Stresino)

1. Confirmed understanding of SO_x and hydrocarbon regulations.
2. 2 out of the 4 refineries with FCC's are believed to have CO boilers.

2. TELEPHONE CONVERSATION SUMMARIES Continued

Kansas (Robert Wallace)

1. Confirmed understanding on no source performance standards for SO_x and hydrocarbons. There has been hydrocarbon monitoring which led to a decision that no regulation was necessary and there is thought of an SO_x regulation.
2. The refinery with an FCC in Kansas County does have a CO boiler.

Louisiana (Orey Tanner)

1. Confirmed understanding of SO_x regulation and existence of no hydrocarbon regulation.
2. Of the 9 FCC facilities in Louisiana, well over half have CO boilers. The Good Hope refinery, which does not have one, uses a new DuPont catalyst and claims its CO emissions are low enough not to need control.

Until hearing of this DuPont catalyst recently, Tanner would have said the trend was toward increased use of CO boilers.

New Jersey (Tom Leonard)

1. Confirmed understanding of SO_x regulation and existence of only an ambient air quality standard for hydrocarbons. Sulfur content in fuel regulation is different for commercial and non-commercial fuels. Refineries can be under either classification, but generally are considered non-commercial.
2. All 4 units in New Jersey have CO boilers.
3. Hydrotreating is used by all 4 units in New Jersey.

Ohio (Howard Johnson)

1. Confirmed understanding of SO_x regulations and existence of no hydrocarbon regulation.
2. 5 of the 6 units in Ohio have CO boilers.

2. TELEPHONE CONVERSATION SUMMARIES Continued

Oklahoma (John Drake)

1. Confirmed understanding that there are no SO_x or hydrocarbon regulations applicable to FCC's.
2. Well over half of the 10 FCC units in the state have them.

Pennsylvania (Frank Willard)

1. Confirmed understanding of SO_x regulation and existence of no hydrocarbons regulation for FCC's.
2. At least 2 of the 4 units in Pennsylvania have CO boilers. They are very old and malfunction frequently.
3. Both the facilities with CO boilers also have hydrotreating.

Texas (Frank Spuhler)

1. Confirmed understanding of regulations.
2. Most of the 30 facilities have CO boilers. A lesser amount use HTR (particularly the newer ones). Spuhler feels CO boiler use is on the increase.

Washington (Michael Landor)

1. Confirmed understanding of SO_x regulation and existence of no hydrocarbon regulation.

2. TELEPHONE CONVERSATION SUMMARIES Continued

b. Other Telephone Conversation Summaries

Davison Chemical (Albert Chatard)

1. Data on catalytic cracker feed hydrotreating can be found in The Oil and Gas Journal, Annual Refinery Survey.
2. Chatard has no information on CO boiler installations.
3. An upper limit growth projection for FCC capacity is 2 - 2-1/2% per year. There is considerable uncertainty regarding gasoline demand, which is the key to growth.

Jim Montgomery

We spoke to Montgomery in the absence of Mr. Blazek, who regularly sits on the NPDA Q and A Committee.

1. Hydrotreating of FCC feedstock - Montgomery thought about 10% of FCC feedstocks are hydrotreated. He believes the majority of this capacity would be in California, due to the high nitrogen content of the indigenous crudes.
2. CO boilers - Montgomery believes that about 2/3 of all FCC units have CO boilers, particularly the larger ones. This would make an aggregate capacity of about 67%.
3. FCC capacity growth - Not much information.
4. CO promoter catalyst - Montgomery told us that the new catalysts promote CO oxidation in the dense bed region where there is an adequate heat sink and less chance of local overheating and potential de-activation of the zeolite catalyst. Without the promoter catalyst, the maximum temperature occurs in the dilute phase where the metallurgy of the intervals may not be adequate.
5. HTR - There are two reasons for applying HTR: 1) to reduce CO emissions to <500 ppm, and 2) to improve catalyst regeneration which allows conversion or capacity to increase. Montgomery estimated that there are from 32-34 units using HTR which he roughly estimates as 750-900 MBPD of fresh feed capacity.
6. Davison catalyst - Approximately 21 units representing about 300-375 MBPD of capacity, using the Davison catalyst.

2. TELEPHONE CONVERSATION SUMMARIES Continued

and, therefore, must be purged from the system. A crystallizer is used to purge sodium sulfate. The waste solids are generally 85% sodium sulfate and 15% sodium sulfite and bisulfite. Thus, the sodium makeup to the Wellman-Lord system should be greater than the oxidation plus SO_3 absorption in the system.

In the application of the system to utility boilers, the flue gas generally contains very little SO_3 and has, on the average, 4% oxygen. This combination results in the oxidation of 10% of the SO_2 absorbed.

The flue gas from the FCC units contains 1-2% and the SO_3 varies widely. If the SO_3 is present in a large quantity and is absorbed in the Wellman-Lord system, it will result in large losses of sodium.

The system has very little absorption capacity for NO_x .

2. TELEPHONE CONVERSATION SUMMARIES Continued

Exxon Research and Engineering Company (Terry Day)

Exxon is presently updating FCCU capital investment estimates for their technical literature. Previous estimates were \$375-450/daily barrel of fresh feed, based on second quarter 1973 USGC prices and a 35,000 BPD unit. The estimate includes direct M&L for the reactor, regenerator (including blower) and fractionation. As a rough guess, the regenerator is ~40% of the total cost. The total erected cost (TEC) would be about 2 times M&L.

Revamping for HTR in most cases would not cost as much as 50% of the TEC of the regenerator. If a new blower were required, the revamp costs could be close to 50%.

Davy Power Gas (Chris Earl)

We spoke to Chris Earl about the application of the Wellman-Lord system for FCC units. Most of the material in connection with the operation of the Wellman-Lord system and the economics of the system are available in our files. Therefore, the conversation was a short one and only a few questions were asked.

1. The Wellman-Lord technology is available for application. Normally, the systems are owned by Davy-Power Gas, and the users pay the fee for gas cleanup. The system has not been applied to FCC units; therefore, no operating information on the Wellman-Lord system on FCC units is available.
2. The Wellman-Lord system is a fully-developed SO₂ control system for commercial application. There are about one dozen systems either in the planning stage or under construction. Most of these applications are for sulfuric acid plants or coal- or oil-fired utility boilers. The availability of the system is generally high, >90%, and there are no major operating problems.
3. In the application of the Wellman-Lord system to the FCC units the major question is of oxidation. The emissions from the FCC units may contain from 0-65% of the SO_x, as SO₃. If the SO₃ is present above the condensation point, it will be present as a vapor form and will be absorbed in the liquid phase. However, if the SO₃ is present in the mist form, it will not be captured in the precleaner of the Wellman-Lord system and will escape through the system. The Wellman-Lord system has a precleaner which removes large particles. The precleaner has a low pressure drop and, therefore, is not effective on condensation type of nuclei. The purpose of the precleaner is to ensure that no particles are captured in the SO₂ absorption section.

In the Wellman-Lord system, the absorption of SO₃ or oxidation of sodium sulfite results in the formation of sodium sulfate. The sodium sulfate is not regenerated in the Wellman-Lord system

APPENDIX D
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BIBLIOGRAPHY

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APPENDIX E

TRC MODEL IV

Several models have been developed by the EPA for the determination of priorities over the past few years. The first model provided a comparison of source categories based on total atmospheric emissions of all pollutants, availability of control technology, and other factors. The second model focused on the need for individual priorities for each pollutant and attempted to restrict rating criteria to factors selected from a generalized strategy for the pollutant. Impact on emissions was a prime criterion in all cases, but impact was expressed on a relative scale. The third model attempted to emphasize impact, but the relative scale concept was retained. Because impact was expressed in a relative way, the model did not provide a system amenable to gradual refinement as available information was improved. Other models, developed by EPA, have taken into account toxicity, exposure, ambient air concentrations or population density. These models are generally complex and not amenable to modification or refinement in addition to presenting impact on a relative scale.

Model IV, which is developed below, is amenable to data refinement and provides a quantitative estimate of anticipated impact of standards of performance in preventing atmospheric emissions.

The additional control potential of new or revised standards of performance stems from the application of emission standards that are more stringent than those presently applied to construction and modification. This potential, for a specified time period, is expressed as

$$(T_S - T_N)$$

Where: T_S = Emissions under baseline year control regulations

T_N = Emissions under new or revised standards of performance.

To calculate the control potential of standards of performance, other factors must be considered, such as the portion of growth requirements that can be satisfied from present unused capacity and the obsolescence and replacement rates of existing facilities. Such a comparison can be expressed mathematically.

The following notation is used in the development of the relationship between projected emissions under baseline year (1975) regulations and NSPS control.

T_S = total emissions in i^{th} year under baseline year regulations
(tons/yr)

T_N = total emissions in i^{th} year under new or revised NSPS which
have been promulgated in the j^{th} year (tons/yr)

T_U = total emissions in i^{th} year assuming no control (tons/yr)

T_A = total emissions in baseline year under baseline year regulations
(tons/yr)

K = normal fractional utilization rate of existing capacity,
assumed constant during time interval

A = baseline year production capacity (production units/yr)

B = production capacity from construction and modification to
replace obsolete facilities (production units/yr)

C = production capacity from construction and modification to in-
crease output above baseline year capacity (production units/yr)

P_B = construction and modification rate to replace obsolete capacity
(decimal fraction of baseline capacity/yr)

P_C = construction and modification rate to increase industry capacity (decimal fraction of baseline capacity/yr)

E_S = allowable emissions under existing regulations (mass/unit capacity)

E_N = allowable emissions under standards of performance (mass/unit capacity)

E_{11} = emissions with no control (mass/unit capacity)

For the purpose of this study the i^{th} year is defined as 1985 and the j^{th} year, 1975.

Assuming that capacity lost due to obsolescence is replaced by construction and modification, as schematically shown in Figure 5-1, then,

$$T_S = E_S K (A - B) + E_S K (B + C) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$T_N = E_S K (A - B) + E_N K (B + C) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$T_S - T_N = K (B + C) (E_S - E_N) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Values of B and C are determined as follows:

(a) If compound growth is assumed,

$$B = A [(1 + P_R)^i - 1] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$C = A [(1 + P_C)^i - 1] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(b) If simple growth is assumed,

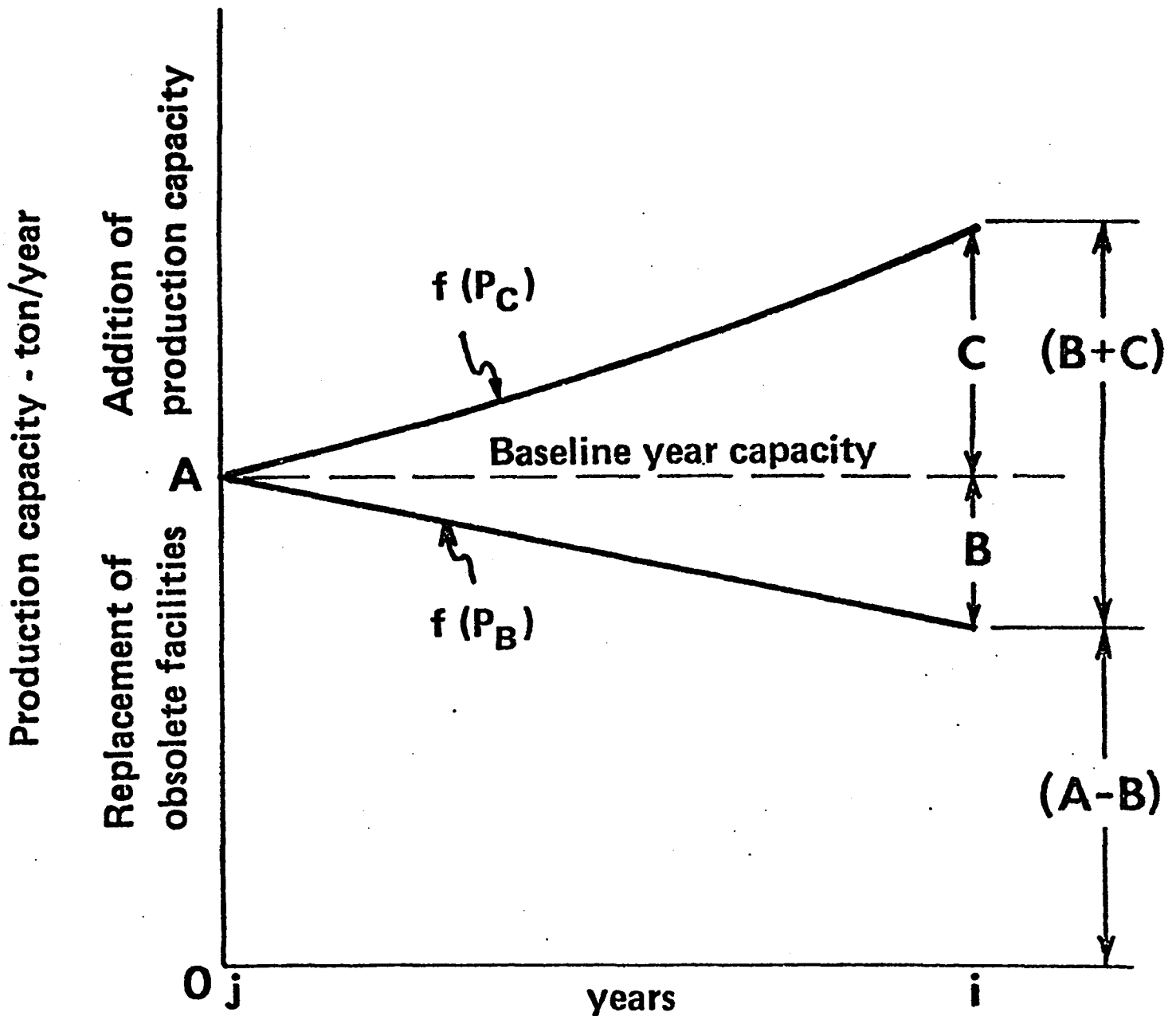
[illegible]

$$C = \text{AiP}_{\phi} (7)$$

where

i = elapsed time, years

Applicability of NSPS to construction and modification



$(A-B)$ = capacity regulated by existing limitations

$(B+C)$ = capacity regulated by NSPS

In addition, the following values may be calculated:

$$T_A = E_S K A \quad (8)$$

$$T_U = E_U K (A - B) + E_U K (B + C) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Further refinement of the Model may be realized for cases where E_S for new and existing plants differ. In this case,

$$T_S = KE_{S_1} (A - B) + KE_{S_2} (B + C) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where:

$$E_{S_1} = E_S \text{ for existing plants}$$

$$E_{S_2} = E_S \text{ for new plants}$$

Therefore,

$$T_S - T_N = K (B + C) (E_{S_2} - E_N) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Section 111 (d) of the Clean Air Act requires the States to regulate designated pollutants from existing installations for industries to which NSPS have been applied. To handle this situation, a slight modification to the model is necessary. T_U , T_A and T_S are the same as for criteria pollutants. T_N is redefined, however, as

$$T_{ND} = E_{III}(d) K (A - B) + E_N K (B + C) \dots (12)$$

Where:

$E_{111(d)}$ = allowable emissions under State regulations as required by Section 111(d) of the Act.

T_{ND} = total emissions in i^{th} year under Section 111(d) and NSPS regulations.

Due to the large number of calculations to be performed and the repetitive nature of these calculations, the model has been computerized. A printout of the program can be found in Appendix III.

For the purposes of this study, K , A , P_B and P_C are defined as industrial prime variables. E_S , E_U , E_N and E_{III} (d) are defined as emission prime variables. T_A , T_U , T_S , T_N , T_{ND} , B and C are referred to as intermediate variables.

5.3 INDUSTRIAL FACTORS

5.3.1 Normal Fractional Utilization - K

The variable, K , represents that fraction of total existing capacity which is brought into service to produce a given output. By applying this factor to the capacity based values of A , B and C , impact on emissions is determined for actual production. The numerical value of K may be arbitrarily changed to permit a reevaluation of impact on emissions at any production level, if so desired. It is for this reason that K exists within the Model.

K was generally deduced from information available in the literature by simply dividing production by capacity. Occasionally, a direct reference to the value was made. Although the definition appears to be relatively straightforward, the actual value can be interpreted several ways based upon the original definition of the term capacity. Industries generally specify their production capacity in two ways--preferred or physical.⁽⁴⁾ Physical capacity is defined as the maximum production that would result if an industry pushed its output to the ultimate practical level. Preferred capacity, on the other hand, is the maximum quantity of production that would result considering equipment limitations, normal operating schedules, maintenance, shutdowns and profits.

Although the values of K were determined from many data sources within the literature, several were exceptionally valuable. The Chemical Economics Handbook⁽⁵⁾ gave production and capacity information for many industrial categories as well as breakdowns of various processes or methods within the industry. A great deal of information necessary to develop K was obtained from draft and final reports made available by EPA. In some cases, Department of Commerce Publications, such as the Census of Manufacturers⁽⁶⁾ and the Survey of Current Business⁽⁴⁾, were used.

Determination of K for industrial categories that had associated production and capacity data was relatively straightforward. A few source categories, however, did not have an associated production rate and had to be treated differently. Field burning of sugar cane, for example, is a "do or don't" situation. Therefore, K was set equal to unity for this type of process. Emission factors for the dry cleaning industry were developed on a per capita basis with the values of A, B and C being related to population. Since population is, in fact, "capacity", K was set equal to unity. In general, the majority of manufacturing processes had a fractional utilization greater than 0.7. Most were in the 0.8 to 0.9 range.

5.3.2 Production Capacity - A

The variable, A, is defined as industrial production capacity in the baseline year, 1975. It is used to derive the values of new (C) or replaced (B) capacity in 1985 (Equations 4 through 7) and to define existing capacity in 1985 not subject to NSPS ($A - B$). Production capacity was generally determined from production data found in the literature for

some year other than 1975. This value was converted to capacity in 1975 by dividing by fractional utilization, K, and scaling this value by P_C to 1975. For those cases where actual capacity was quoted in the literature, it was not necessary to divide by K.

The units for capacity were selected to be consistent with those used by the specific industry and which were compatible with the other factors. In most cases, tons of product or tons of feed per year were chosen. However, for the phosphate fertilizer industries, tons of P_2O_5 per year was chosen since production and capacity information is commonly quoted on this basis. For combustion sources, A was expressed in BTU's or horsepower - years per year. For incinerators, tons of refuse handled annually was specified. Occasionally, the value of capacity was chosen in terms of a quantity to which emission or growth factors could be related. An example of this is degreasing for which tons of metal cleaned, not the quantity of solvent used, was selected. Tons of clothes cleaned annually was chosen as the basis for the dry cleaning analysis. A growth rate within the industry based on anticipated population trends could then be employed.

The most recent production or capacity data available was used so that extrapolation to the baseline year would result in as realistic a value as possible. In nearly all cases, data sources were more recent than 1967; much data were from the 1970's. Several sources were exceptionally valuable, notably those mentioned previously in the discussion regarding fractional utilization. Others included the Chemical Profiles series⁽⁷⁾, Particulate Pollutant System Study⁽⁸⁾, EPA control techniques documents and Hydrocarbon Pollutant Systems Study⁽⁹⁾.

5.3.3 Increase in Industrial Capacity Over 1975 Capacity - P_C

The variable, P_C , is defined as the average anticipated growth rate in industrial capacity during the period 1975 to 1985. It is expressed as a fraction and is applied to A, production capacity, to determine C, (Equations 5 and 7). It is this value of C to which NSPS can be applied.

P_C was determined by several methods, the most general being extrapolation of historical production or capacity data to the year 1985. A second relatively common approach was to relate the anticipated number of new plants and the average new plant capacity to 1975 capacity levels. A third alternative was based on "expert predictions" from sources such as Department of Commerce, associated trade associations, cognizant industry personnel or from studies performed by a number of organizations such as the Stanford Research Institute ⁽⁵⁾ or the Environmental Protection Agency. For industries whose function is directly related to population, Department of Commerce data regarding population trends was employed to determine P_C .

A growth rate based on "expert predictions" or extrapolation of data for the ten year period, 1975 to 1985, is subject to the many biases which could occur during that period. For example, availability of raw materials, sudden changes in demand or consumption patterns or economic factors such as cost of money and price controls could alter historical trends or invalidate "expert predictions". As a result, the impact of standards would be subsequently altered.

As shown in Equations 5 and 7, P_C may be expressed as either a compound or simple growth rate. If the historical growth pattern was indeed compound in nature, the value of P_C was calculated by the following equation:

$$P_C = \sqrt[x-y]{\frac{\text{Capacity in year "x"}}{\text{Capacity in year "y"}}} - 1.0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where $x > y$

If the historical growth pattern was simple in nature, the value of P_C was calculated by the following equation:

$$P_C = \frac{\text{Capacity in year "x"} - \text{Capacity in year "y"}}{(x-y) \text{ Capacity in 1975}} \quad . \quad . \quad . \quad . \quad (14)$$

where $x > y$

For the case of simple growth, it is necessary to relate the growth to the baseline year, 1975, as shown above. For compound growth, the rate can be applied to any year.

For the majority of cases, P_C was approximated by a compound rate and based on the most recent data available to preclude major inaccuracies in the determination of emission impact.

There were several cases where the anticipated growth rate exceeded 10% annually. Industries characterized by both a rapid growth rate and significant emission rates are prime candidates for NSPS since almost complete control of the industry can be recognized in a relatively short time period. Since this rapid growth rate will eventually level off, the use of the Model should not be extrapolated too far beyond the baseline year or an unrealistic value of emission impact could result. Future growth rates in these industries should, therefore, be carefully monitored.

For several industries such as lead pigment manufacture or ROP triple superphosphate production, a continuing downward trend in capacity was noted. This characteristic was associated with industries being phased out due to replacement by more efficient processes, or the demand for whose product was declining because of the availability of a better or cheaper product. For the purpose of our study, we assumed that these industries did not replace obsolete facilities due to the lack of economic incentive. Accordingly, there would be no new or modified capacity generated between 1975 and 1985 that could be controlled by NSPS. However, under Section 111d of the Clean Air Act, the States are required to regulate designated pollutants from existing installations for industries to which NSPS have been applied. It was necessary, therefore, to determine T_S , T_{ND} and $(T_S - T_{ND})$ for those sources with decreasing production capable of emitting designated pollutants. Values for the year 1985 are included in Section 6.0, Presentation of Results. In addition, values for each year between 1975 and 1985 are presented in Section 7.0, Analysis. This has been done since the emission impact is greatest in 1976 and diminishes throughout the ten year period due to the decreasing capacity.

For several other industries, a zero growth rate was observed. We assumed, however, that obsolete facilities were replaced, thereby permitting an emission impact calculation to be performed on the value B, the obsolete production capacity replaced between 1975 and 1985.

5.3.4 Replacement Rate of Obsolete Production Capacity - P_B

The variable, P_B , is defined as the average rate at which obsolete production capacity is replaced during the period 1975 to 1985. It is expressed as a fraction and is applied to A to determine B, (Equations 4 and 6). It is this value of B to which NSPS can be applied. Also, the quantity, (A-B), defines the existing production capacity in 1985 to which only State regulations are applicable.

P_B was determined by one of three methods. One approach was to relate the number of known or estimated plant closings and the average existing plant capacity to 1975 capacity levels. A second method was based on known equipment lifetime. For example, if a major piece of production equipment had an actual estimated lifetime of 50 years, it would depreciate at a rate of 2% per year on a simple basis. The third, and most common, method was to use depreciation guidelines published by the Internal Revenue Service⁽¹⁰⁾. The allowance permitted by the IRS is an economic factor used for tax collection purposes and generally depreciates equipment and facilities over a shorter term than their actual useful life. We assumed for the purpose of this study, therefore, that typical equipment and facilities within each industrial category evaluated had a useful life equal to twice that allowed by the IRS. As a general rule, P_B was based on very limited data and, as a result, a great deal of judgment was necessary. For this reason, P_B was selected on the basis of straight line depreciation (simple) to avoid compounding potential errors.

5.4: EMISSION FACTORS

5.4.1 Uncontrolled Emission Factor - E_U

The variable, E_U , is the emission factor representing a condition of no control. It is used to calculate T_U , the uncontrolled emissions in 1985, the value to which T_S and T_N may be compared to determine the nationwide impact on emissions of regulations in general. E_U is also employed to develop E_N , the NSPS controlled emission factor. When the efficiency of a control device is stated, application of this efficiency to E_U results in the calculation of E_N . Thirdly, E_U replaces the value of E_S , the emission factor representing control to the extent required by State regulations, when no regulations for an industry exist in a given state.

E_U , in most cases, represents a totally uncontrolled emission factor. On occasion, however, it represents the controlled emission factor at the exit of a control device if such a device is integral with the process. An example of this would be carbon black manufacture by the furnace process where the product is actually collected by a series of control devices. If these devices were not functional, the process could not operate.

Determination of E_U was relatively straightforward and references in the literature were abundant. Compilation of Air Pollutant Emission Factors, AP-42⁽¹¹⁾ and Air Pollutant Emission Factors⁽¹²⁾ were major reference sources for this value. Uncontrolled emission factors for particulates were determined for many sources from the Particulate Pollutant Systems Study⁽⁸⁾. Occasionally, E_U for a specific process or operation was synthesized from several independent values of E_U . Examples were fossil fuel fired boilers, gas turbine engines and internal combustion engines where the value of E_U was determined by weighting the emission factors for each fuel type by the

fraction of the total heating value supplied by each fuel. For certain industries, E_U was synthesized by weighting the emission factors from different portions of an operation by the fraction of total capacity associated with that operation. It is for this reason that the value of E_U developed for this study should not be used in any other context or erroneous conclusions could result.

Units for E_U were chosen to be consistent with the units selected for A , production capacity. For example, if A were in terms of tons of product per year, E_U would be specified in terms of pounds of emissions per ton of product. For those cases where literature quotations for E_U were on a different basis than A , it was necessary to make the proper conversion. Generally speaking, emission factors for fugitive emissions were not included within the study even though for certain industries fugitive emissions may be greater than emissions from point sources. This is an area where further study is necessary to quantitatively assess the importance of this category of sources and to develop methods for emission control.

5.4.2 Controlled Emission Factor - E_N

The variable, E_N , is the emission factor representing the condition of best control applied to new sources. It is used to determine T_N , the emissions that would exist in 1985 if NSPS were applied. When T_N is subtracted from T_S , the quantitative value of emission impact is determined. The units of E_N were chosen to be consistent with those selected for E_U .

A literature search was conducted to find the best level of control that could be applied to new or modified construction. The information

came from a wide variety of references. In addition to those mentioned for E_U , which occasionally gave controlled emission factors, the IGCI surveys^(13, 14) and feature articles and process summaries from various trade magazines such as Chemical Engineering were exceptionally valuable. The determination of E_N was accomplished by one of three methods. The first, and most common, was directly from information regarding a well-controlled plant. The second method was by applying a stated control hardware efficiency to the value of E_U . When no reference to control techniques was made, a transfer of technology from similar processes was assumed where it was deemed applicable.

There were several instances where technology to control a specific pollutant within an industry had not been demonstrated and for which a transfer of technology was judged not feasible in our opinion due to technical or economic reasons or for which no control efforts were ever made due to a low associated point source emission rate. For those cases, E_N was developed by assuming the anticipated level of control that would result if present research and development efforts are successful. For those cases where no specific research and development efforts are presently underway, we set $E_N = 0.0$ to determine the maximum hypothetical impact on emissions if the pollutant were to be completely controlled. The purpose of this application was to develop a separate listing of industrial categories, ranked in order of hypothetical emission impact, from which priorities for control technology research and development efforts can be developed. The results are weighted towards categories for which there are no present control efforts ($E_N = 0.0$). They should not be compared to the values determined for the majority of cases where control technology has

been demonstrated or where a transfer of technology was judged feasible. This listing is therefore presented separately in Tables 6-1 through 6-13.

The values of E_N determined for this study were based on present levels of control technology as determined from the literature. It is possible, however, that nationwide plant surveys for each industry could locate more efficient techniques for unique installations which have not been presented in the literature. Such an effort was beyond the scope of this project. It is also recognized that advancements in the state-of-the-art of control technology will occur and the value of E_N , will consequently change as time goes on.

5.4.3 Controlled Emission Factor For Designated Pollutants - $E_{111(d)}$

The variable, $E_{111(d)}$, is the emission factor which represents best control applied to designated* pollutants from existing plants. It is used to determine T_{ND} , the emissions of a designated pollutant that would exist in 1985 for existing plants under State control and new plants under NSPS. Section 111(d) of the Clean Air Act^(2,3) requires the States to draft, maintain and enforce regulations for the control of designated pollutants from existing sources for which NSPS have been set for new sources within that industry. As a result, the Model was modified to reflect this situation (see Equation 12). When T_{ND} is subtracted from T_S , the quantitative

*For the purpose of this study the following pollutants are defined as designated: fluorides, trace metals, acid mist, lead, ammonia, sulfides, chlorine and odors.

value of emission impact for designated pollutants is determined. Units are identical to E_N .

Determination of $E_{111(d)}$ was accomplished in a manner similar to E_N . Control techniques or levels, however, differed in that retrofit technology was necessary for existing plants. In most cases, we believe that available control technology for new installations could also be retrofit to existing installations. Of course, there would be specific instances at certain individual plants where this might not be possible due to existing structures and prohibitive costs.

Equation (12) was also used to calculate controlled emissions of "hazardous" pollutants as defined in Section 112 of the Clean Air Act. However, $E_{111(d)}$ was replaced by E_N , since both new and existing sources would be controlled.

5.4.4 Estimated Allowable Emission Under 1975 Regulations - E_S

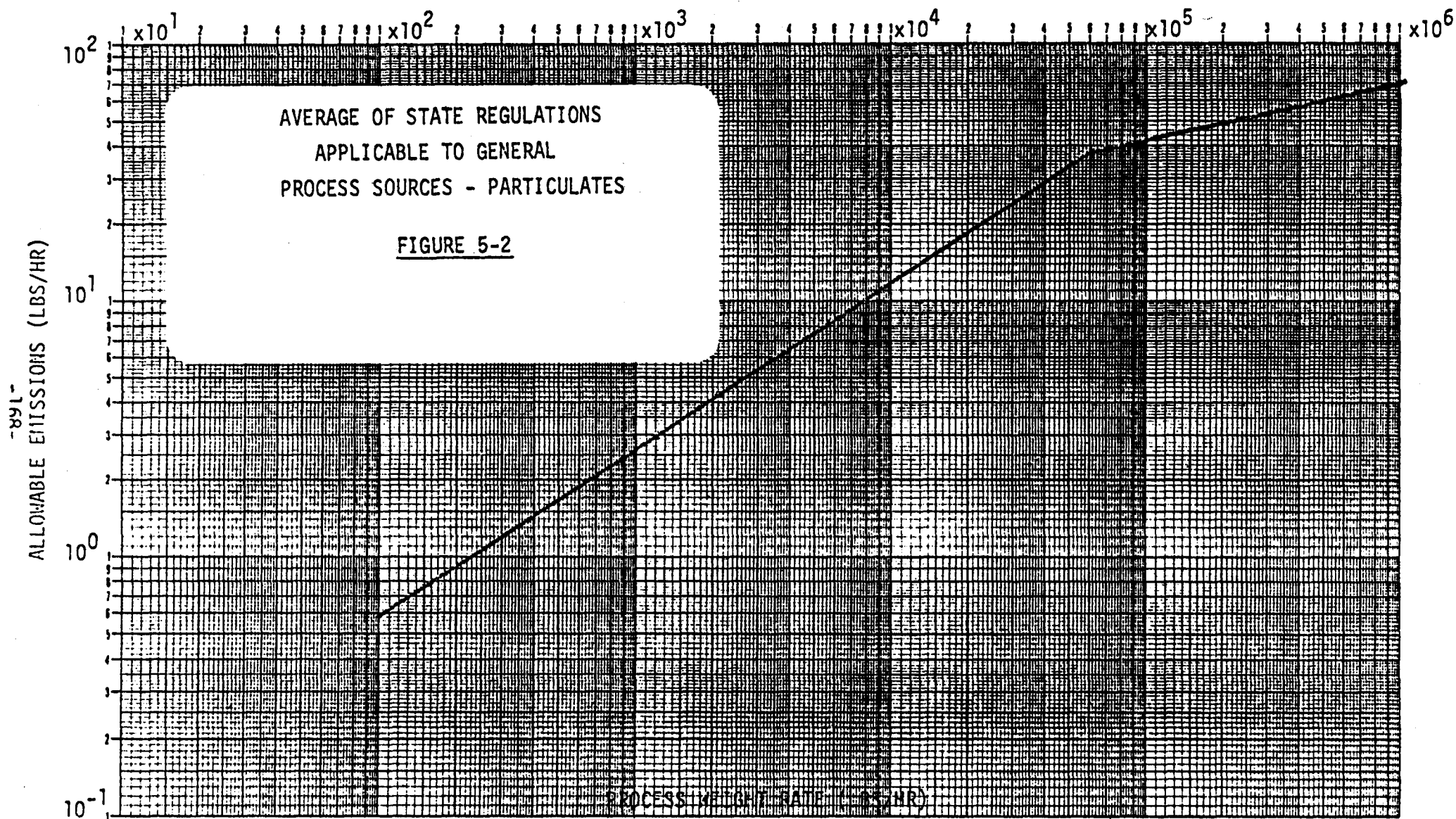
The variable, E_S , is the emission factor which represents the 1975 level of control required under State, local, regional or Federal regulations. It is used to determine T_S , emissions in 1985 under baseline year regulations. When T_N is subtracted from T_S , the quantitative impact of NSPS on emissions is calculated.

To determine the applicable regulations, tabulations were made on a State by State, pollutant by pollutant, and industry by industry (where applicable) basis. This was done by updating and augmenting all summary tables published in Analysis of Final State Implementation Plans⁽¹⁵⁾ (to August 1974) by reviewing all the State regulations as published in the Environment Reporter⁽¹⁶⁾. Federal regulations for new sources promulgated under Section 111 of the Clean Air Act were also incorporated. Ready access to all regulations was thereby provided in tabular form. No effort was made to account for anticipated state regulations beyond 1975.

verted output to input capacity--the value required by the process weight rate curve. The allowable emission in pounds per hour from the curve was divided by the output capacity to obtain E_{S_i} in proper units. When these calculations had been made for each State of concern, the average value of E_S was determined as described by Equation (15). This is a typical example of E_S determination. There were many variations and special case situations too numerous to mention here. Details of the various calculations for each industrial category can be found in the appropriate Appendices.

There were many cases where sources of particulate emissions were distributed throughout all States and specific data regarding geographical distribution was lacking. For these cases, we developed a generalized process weight rate curve by linearly averaging the process weight curves of all the States at each production level. The resulting curve is presented in Figure 5-2. It is slightly less stringent than the curve originally issued as the EPA guideline and slightly more stringent than a curve generated by weighting the process weight curves of the twenty-five most populated States on the basis of fractional population distribution. Similar generalizations were developed for the particulate, NO_x and SO_x regulations for fuel burning sources.

For hydrocarbon emission sources, the value of E_S is related to the reactivity of the pollutant since different regulations apply to reactive and non-reactive hydrocarbons. For the case of reactive emissions, we determined the typical plant size within each state of concern, calculated the hourly emission rate and applied the "percent control" regulation, if it existed, to determine whether the hourly or "percent control" emission regulation was applicable. After converting the result for each State to



pounds per ton, a weighting process, as shown in Equation (15) was performed. As was the case for general process particulate emission E_S determination, there were many variations and special case considerations too numerous to mention here. Details of the various calculations for each industrial category can be found in the appropriate Appendices.

For several cases, State regulations for new sources differed from existing sources. Consequently, two values of E_S were determined and applied to the Model as shown in Equation (10).

Regulations pertaining to visible emissions were not included in the evaluation of E_S due to the impracticality of converting stated opacity levels to a weight rate of emissions for use in the Model.

APPENDIX F

RELATIONSHIP OF PAD DISTRICTS TO AIR QUALITY CONTROL REGIONS

In this study we have looked at the U.S. FCC capacity in terms of PAD Districts of which there are 5 (see Figure F-1). Another way in which the FCC population can be categorized is by Air Quality Control Regions, of which there are 10 (see Figure F-2). The relationships between these two categorizations are shown by state in Table F-1.

PETROLEUM ADMINISTRATION FOR DEFENSE (PAD) DISTRICTS

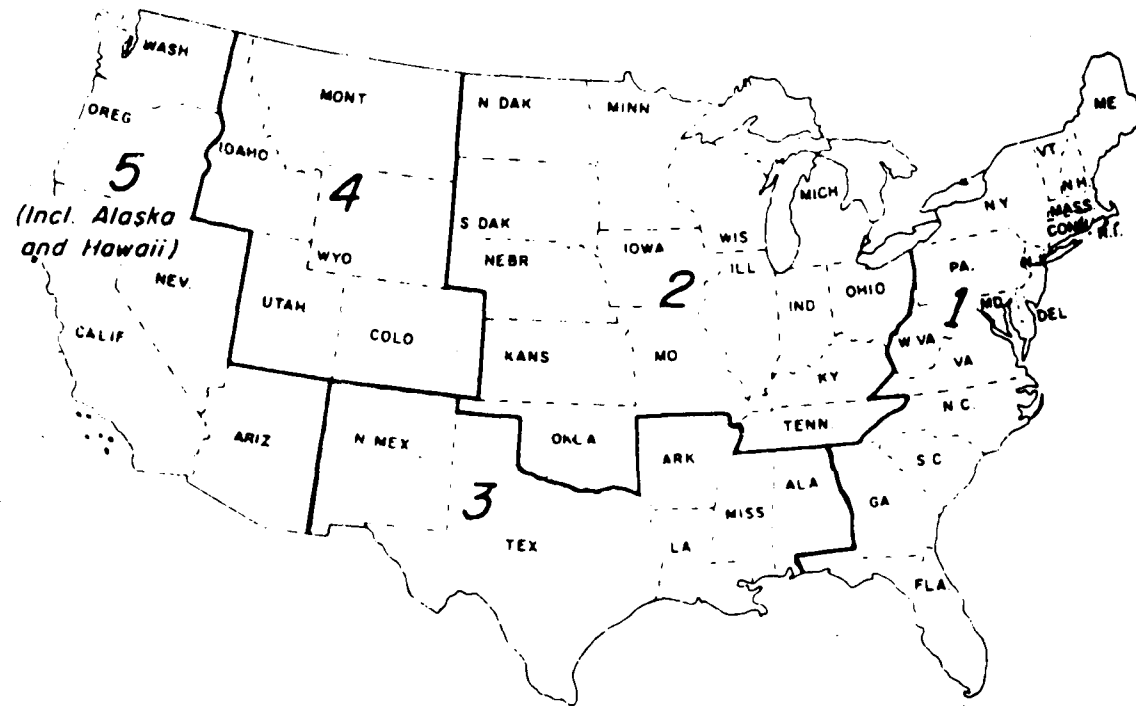


FIGURE F-1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Regional Offices

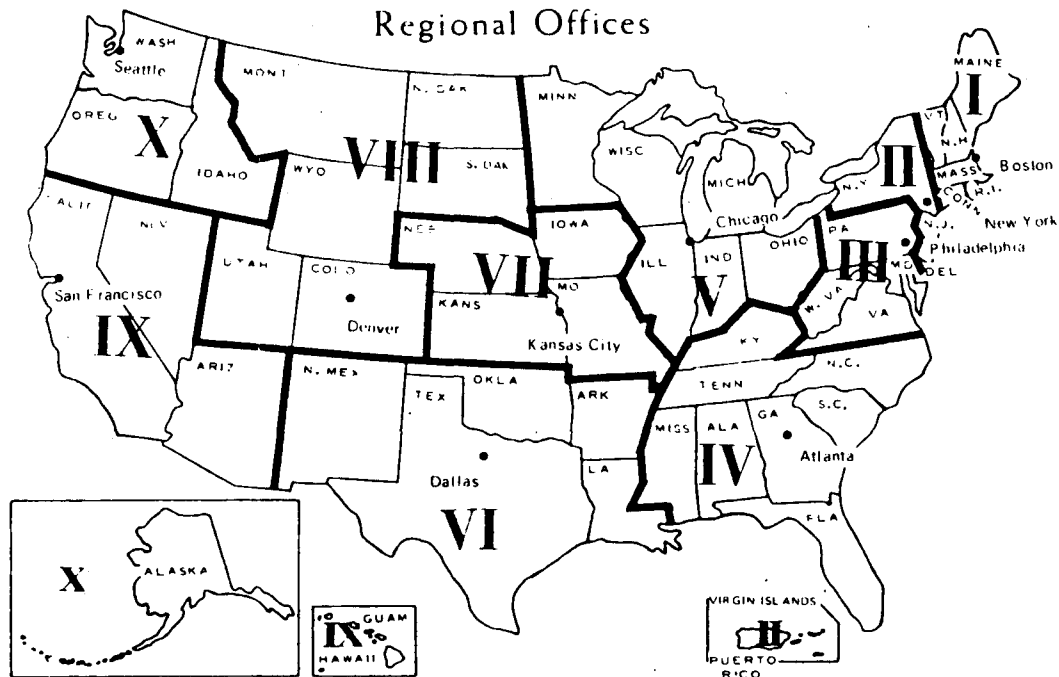


FIGURE F-2

TABLE F-1

U. S. PETROLEUM REFINERIES
WITH FCC REGENERATORS

<u>State</u>	<u>No. of Ref. w/FCC</u>	<u>Total Capacity (b/sd)</u>	(January 1, 1976)	
			<u>ACQR</u>	<u>PAD</u>
Arkansas	1	18,000	VI	3
California	13	621,211	IX	5
Colorado	2	23,900	VIII	4
Delaware	1	77,000	I	1
Hawaii	1	23,000	IX	5
Illinois	9	523,277	V	2
Indiana	4	203,800	V	2
Kansas	10	206,450	VII	2
Kentucky	1	55,000	IV	2
Louisiana	9	677,728	VI	3
Michigan	3	46,900	V	2
Minnesota	3	74,500	V	2
Mississippi	2	76,850	IV	3
Missouri	1	53,000	VII	2
Montana	4	72,500	VIII	4
Nebraska	1	2,900	VII	2
New Jersey	4	269,444	II	1
New Mexico	2	17,560	VI	3
New York	2	47,000	II	1
North Dakota	1	34,000	VIII	2
Ohio	6	248,500	V	2
Oklahoma	10	231,675	VI	2
Pennsylvania	4	224,300	III	1
Tennessee	1	13,500	IV	2
Texas	30	1,527,571	VI	3
Utah	6	70,160	X	4
Virginia	1	32,000	III	1
Washington	3	118,600	X	5
Wisconsin	1	10,700	V	2
Wyoming	7	74,078	VIII	4
	<u>143</u>	<u>5,675,104</u>		

Source: Oil and Gas Journal, March 29, 1976.

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>			
1. REPORT NO. EPA-450/3-77-046		3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Screening Study to Determine Need for SO _x and Hydrocarbon NSPS for FCC Regenerators		5. REPORT DATE August 1976	
7. AUTHOR(S)		6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Arthur D. Little, Inc. Acorn Park Cambridge, Massachusetts 02140		8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS U. S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO. 68-02-1332, Task 22	
		13. TYPE OF REPORT AND PERIOD COVERED	
		14. SPONSORING AGENCY CODE 200/04	
15. SUPPLEMENTARY NOTES			
16. ABSTRACT The report quantifies the emissions from a typical Fluid Catalytic Cracking (FCC) unit and identifies and presents all available data that would define the emission levels that can be achieved with the most effective demonstrated control systems for FCC units. In addition, estimated emission reductions that would result through promulgation of new source performance standards for FCC units have been prepared.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Emissions Control Equipment Sulfur Dioxide Carbon Monoxide Hydrocarbons Petroleum Refining		Fluid Catalytic Cracking Regenerator	Air Pollution Content Stationary Sources Hydrocarbon Emission Control Sulfur Dioxide Control Carbon Monoxide Control
18. DISTRIBUTION STATEMENT Unlimited		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 187
		20. SECURITY CLASS (This page) Unclassified	22. PRICE