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ANNUAL CATALYST RESEARCH PROGRAM REPORT APPENDICES Volume I



**Health Effects Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711**

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ANNUAL CATALYST RESEARCH PROGRAM REPORT APPENDICES
Volume I

by

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U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
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Automotive Sulfate Emissions

Summary

The use of oxidation catalysts, starting in 1975, to control hydrocarbon and carbon monoxide emissions from motor vehicles has introduced the potential problem of high localized sulfate levels in the vicinity of multilane highways and in street canyons with relatively stagnant air masses. In non-catalyst equipped vehicles, the sulfur contained in the gasoline is emitted almost entirely as SO_2 . While the SO_2 from automobiles is eventually oxidized to form sulfate, it is usually finely dispersed beforehand and makes up only a small fraction, less than 1%, of the total SO_2 burden to the atmosphere. The scenario for catalyst-equipped vehicles is slightly different. Some of the SO_2 formed in the combustion process is further oxidized to SO_3 by the catalyst. The SO_3 is immediately converted to sulfate which could cause high localized sulfate concentration levels at street level in the vicinity of dense traffic situations.

The purpose of this report is to summarize the results of industry and OMSAPC investigations on sulfate emissions from automobiles and to make conclusions based on these results. (The details of the ORD work are to be summarized in a parallel report). There is not complete agreement on emission levels for various types of catalysts and test conditions, due primarily to two factors. The first factor is storage of sulfates. Sulfates are stored on the catalyst under some operating conditions and released under others. The emission rate of sulfates over any particular period, therefore, is dependent on the previous operating history of the catalyst. The second problem revolves around analytical methods. Considerable progress has been made in these areas and it appears that a consensus is emerging on analytical methods. For these reasons, this report includes much detail about the test conditions and analytical methods to help understand and explain the discrepancies in the data. This understanding is not complete at this time.

Non-catalyst Vehicle Sulfate Emissions.

Non-catalyst equipped vehicles have very low sulfate emission levels according to most investigations. EPA-ORD, GM, Ford and Exxon have reported sulfate emissions to be less than 1% of the fuel sulfur (less than 0.001 gpm), using a generally accepted analytical technique. Chrysler and preliminary EPA-OMSAPC tests, using another analytical method, indicate conversion of 10 to 20% of the fuel sulfur to sulfates. However, this analytical method has not been validated sufficiently for automotive sulfate emissions and may be inaccurate.

Catalyst Vehicle Sulfate Emissions.

Work by GM and Exxon shows that pelleted catalysts have substantially lower sulfate emissions than monolith catalysts, over the EPA Federal Test

Procedure, a low speed urban driving test. This work also shows that sulfates are being stored on the pelleted catalyst under operating conditions found during the FTP. This storage occurs to a much smaller extent on the monolith catalyst which has much less alumina available for interaction with the sulfates. The storage phenomenon for the pelleted catalyst is expected to be a temporary one with later release of sulfur compounds under higher speed driving conditions which result in higher catalyst temperatures. It appears that the stored sulfates might be released as both SO₂ and sulfate.

Work by GM, Ford, and Exxon show pelleted and monolith catalysts to have almost identical sulfate emissions at 60 mph.

Typical emission factors obtained with a 0.03% sulfur fuel, the current national average, are given below:

<u>Driving Schedule</u>	<u>Catalyst</u>	<u>Investigator</u>	<u>Sulfates (gpm)</u>
1972 FTP	Monolith	GM	0.03
	Pelleted	GM	0.009
	Pelleted	GM	0.002
	(No air injection)		
1975 FTP	Monolith	Exxon	0.07
	Pelleted	Exxon	0.02
60 mph	Monolith	Exxon	0.05
	Monolith	Ford	0.06
	Monolith	GM	0.05
	Pelleted	Exxon	0.06
	Pelleted	Ford	0.05
	Pelleted	GM	0.05-0.07

Composite emission factors are as follows with the overall factor based on 65% pelleted and 35% monolith catalysts.

<u>Driving Schedule</u>	<u>Catalyst</u>	<u>Sulfates (gpm)</u>
FTP	Monolith	0.05
	Pelleted	0.01
	Overall	0.02
60 mph	Monolith	0.05
	Pelleted	0.06
	Overall	0.06

The overall estimate for low speed driving conditions of the FTP is somewhat lower than the 0.05 gpm assumed by EPA in the earlier information submitted to the Senate Public Works Committee. The 0.06 gpm value for 60 mph conditions is slightly higher than this 0.05 gpm value.

Sulfate Emission Control.

It is not known to what degree catalyst parameters can be optimized for low sulfate emissions and still have satisfactory HC and CO control. Preliminary results from GM on the cars without air injection are much lower, even at 60 mph for the one test run, than the cars with air injection. Close control of the exhaust oxygen level may result in much lower sulfate emissions. Furthermore, it is not known whether or not automotive sulfate traps are feasible. Investigations are continuing in these areas.

Current Investigations.

The OMSAPC has programs underway to assess control technology for sulfates and obtain characterization data. The ORD is continuing to develop measurement methods, obtain characterization data, do air quality modeling and obtain health effects data. The OAQPS is investigating the feasibility of fuel desulfurization and assisting in the air quality modeling.

The OMSAPC has a contract underway with Exxon Research and Engineering to perform four major tasks in assessing automotive sulfate control technology. Task 1, which is essentially complete, is to conduct a literature search on SO₂ oxidation, SO₃ hydration, kinetics and catalysis of these reactions, and to determine potential trap materials. Task 2 is to assess emissions from non-catalyst vehicles including a 1974 production vehicle, a rotary engine equipped vehicle, a Honda CVCC and a Diesel car. Task 3, to determine factors affecting oxidation of SO₂ will be started as soon as 1975 production vehicles are available. Air injection rate, catalyst formulation, catalyst temperature, and catalyst residence time will be studied. Task 4 is to evaluate the feasibility of sulfate traps. Tests are underway on a calcium oxide trap.

The second OMSAPC contract, being conducted by Southwest Research Institute, is to obtain SO₂ and sulfate emission data on monolith, pelleted, and dual catalyst equipped vehicles, a pre-1973 vehicle, a 1975 non-catalyst car, and Diesel and stratified charge engine equipped vehicles. Sulfate emissions will be measured on the two oxidation catalyst equipped vehicles through 15,000 miles.

The scheduled completion date for both contracts is March, 1975.

The OMSAPC in-house work is directed towards determining sulfate emission factors. Measurements are made over the 1975 FTP, the Hiway Economy Cycle and at 60 mph steady state. Twelve vehicles have been tested to date,

1975 GM and Ford catalyst prototypes, a Gould dual catalyst vehicle at 0 and 25,000 miles, Mercedes and Peugeot Diesels, a Dresser carburetor equipped vehicle, a Honda CVCC, a 1977 Ford catalyst prototype, a Ford stratified charge vehicle with catalyst, a Volvo with three way catalyst and a 1974 Ford without catalyst. Arrangements have been made to continue testing the Volvo three way catalyst vehicle and the 1975 GM catalyst prototype vehicle plus the testing of a Texaco stratified charge vehicle, a 1977 GM catalyst prototype and GM, Ford and Chrysler production vehicles. Future plans include testing of HD Diesels for sulfate emissions.

Automotive Sulfate Emissions

Introduction

The purpose of this paper is to summarize most of the currently available emission data for sulfates from catalyst and non-catalyst vehicles. These data include recent tests run by the automobile and petroleum companies and are in both published literature and information submitted to the Senate Public Works Committee and to EPA. The Senate Public Works Committee held Hearings in November, 1973 on sulfate emissions from catalyst vehicles and received extensive information from various groups including the automobile and petroleum companies. On March 8, 1974, an EPA request for information on automotive sulfate emissions was published in the Federal Register. The automotive, petroleum, and other companies sent extensive test data to EPA in response to this notice. Furthermore, EPA requested reports from the automotive companies on their progress in meeting the 1975-76 automotive standards. In this request, EPA also asked for data on unregulated emissions such as sulfates. These reports, sent to EPA last November, included data on sulfate emissions.

This paper discusses all of the above information and also includes data obtained from tests run by the EPA Office of Mobile Source Air Pollution Control (OMSAPC). Emission data obtained by the EPA Office of Research and Development (ORD) are not included in this report but are included in a separate report parallel to this one.

An EPA report was submitted earlier this year to the Senate Public Works Committee summarizing all data available for sulfates. This paper by the OMSAPC provides additional technical data on some aspects of the report sent to Congress. However, this paper covers only sulfate emissions and does not cover other possible unregulated emissions such as polycyclic organic matter, reactive organics, hydrogen sulfide, platinum, other noble metals, and nickel compounds.

Section 1 - Particulate Emissions

It is important to understand particulate emissions from non-catalyst cars as background before examining particulate and sulfate emissions from catalyst equipped vehicles. Non-catalyst vehicle particulate emissions should be considered for both leaded and unleaded fuel. The following two sections will briefly discuss particulate emissions for leaded and unleaded fuel. These discussions are not meant to be comprehensive (i.e., include all published work) but rather to summarize recent work reported by the automobile companies in their 1973 status reports to EPA and in their testimony before the Senate Public Works Committee in November 1973.

1.1 Particulate Emissions with Leaded Fuel

Non-catalyst type cars, especially older ones (e.g., pre-1971 vehicles) with higher compression ratio engines, have used leaded gasoline which contained an average of about 2.5 g/gallon of lead in the form of lead alkyl compounds. This corresponds to an input to the engine of 0.18 gpm of lead assuming a 13.5 mile/gallon fuel consumption. Approximately 80-90% of this is emitted to the atmosphere with the remainder trapped in the engine and exhaust system. The emitted lead is in the form of various halide and oxyhalide compounds. Thus, about 0.15 gpm of lead is emitted, not including the weight of the halide or oxyhalide part of the compound.

Extensive work done by various investigators and by EPA (both in-house and by contract, such as contracts EHS 70-101 and CPA-22-69-45 with Dow Chemical Company) have shown total airborne particulate emissions from non-catalyst vehicles operated on leaded gasoline to be about 0.25 gpm. Most of the 0.25 gpm are lead compounds. GM cites tests in its progress report showing average emissions of 0.21 gpm (range of 0.13 to 0.33 gpm) for seven vehicles using leaded fuel on the 1972 Federal Test Procedure (FTP).

1.2 Particulate Emissions with Unleaded Fuel

Most 1971 and later cars can use lower octane low lead or unleaded fuels. Some manufacturers, such as GM, recommend the use of such gasoline in their newer cars. Particulate emissions from non-catalyst cars using unleaded fuel are substantially lower than leaded fuel.

EPA tests at Dow Chemical show particulate emissions with unleaded fuel to be about 0.01-0.02 gpm under either 30 or 60 mph steady state or a cold start type test. These particulates consist of carbon and various higher molecular weight organic compounds. GM mentions that six cars tested on the 1972 FTP showed an average emission of 0.03 gpm (range of 0.015 to 0.04 gpm). Ford cites a recent test done at a program they sponsored at Battelle Laboratories showing a 0.01 gpm emission factor for a car using unleaded fuel at 60 mph steady state.

1.3 Particulate Emissions from Catalyst Vehicles with Unleaded Fuel

Much less work has been done on total particulate emissions from catalyst-equipped vehicles although sulfate emissions have received much more attention. The major work in this area was done by EPA through a contract with Dow Chemical Company (EHS-70-101). Several catalysts were tested on an engine dynamometer, and several catalysts were tested on vehicles. Both noble metal monolith and base metal pelleted catalysts were tested. There is some variation in particulate emissions from test to test. However, generally the total particulate emissions with the catalyst and unleaded fuel were far less than those obtained for non-catalyst cars with leaded fuel but greater than those found for non-catalyst cars with unleaded fuel. Typical particulate emission levels for the Engelhard monolith noble metal

catalyst were about 0.03-0.08 gpm under either steady state conditions (30 or 60 mph) or a cold start test. The emissions for the pelleted catalysts tested were lower at approximately 0.02-0.05 gpm under the same conditions. Ford work at Battelle Laboratories with noble metal monolith shows particulate emissions of 0.12 gpm at 60 mph steady state.

These emission results and those mentioned earlier in Section 1 are summarized in Table 1.

Section 2 General Aspects of Sulfate Emissions

The sulfur in gasoline (about 0.03% by weight) oxidizes to SO_2 in the combustion process with very minute quantities of SO_3 also being formed. It is important to note that on a national average SO_2 emissions from motor vehicles are less than one percent of total SO_2 emissions from man made sources. Atmospheric SO_2 is slowly oxidized to SO_3 . However, automotive oxidation catalysts apparently increase the amount of SO_3 directly emitted from motor vehicles and may result in high localized sulfate levels.

Increased sulfate emissions from catalyst equipped vehicles were discovered in 1972 in an analysis Ford did on particulate samples collected by Dow under Contract EHS-70-101 with EPA. These samples were collected from a vehicle equipped with an Engelhard noble metal monolith oxidation catalyst. Abnormally high particulate emissions were obtained on this Ford car even though it was operated with unleaded fuel. Some of the samples were sent to Ford for detailed analysis which showed sulfuric acid. Since this initial finding at the end of 1972, more extensive characterization of sulfate emissions has been done by various groups including the OMSAPC and the ORD of EPA, General Motors, Ford, Chrysler, and Exxon Research. The results of this work, with the exception of the ORD work which is covered in a separate report, will be summarized in the following sections.

The purpose of this work was not only to obtain sulfate emission factors but also to determine what parameters affect sulfate emissions. Parameters that could possibly affect sulfate emissions from catalyst equipped vehicles include catalyst type (base or noble metal), catalyst substrate (pellet or monolith), catalyst mileage, catalyst location, catalyst operating temperature, and air injection rate. For example, a fresh catalyst with higher activity may result in increased SO_2 oxidation compared to a catalyst with high mileage. Also, catalyst temperature may affect SO_3 formation since the SO_2 - SO_3 equilibrium shifts more to SO_2 at higher temperatures.

In addition to these factors, it is possible to "store" SO_3 on a catalyst by reaction with the alumina type substrate. This storage could occur in one driving condition, such as low speed driving with subsequent release in another condition such as high speed driving. High speed driving results in higher catalyst temperature which could decompose the aluminum sulfates formed at lower temperatures. It is also possible to store and later release

TABLE 1
Particulate Emissions with Lead or Unleaded Fuel

<u>Control System</u>	<u>Fuel</u>	<u>Data Source</u>	<u>Driving Condition</u>	<u>Emissions (gpm)</u>
Non-catalyst	Leaded	EPA	Various	0.25
		GM	1972 FTP	0.21
Non-catalyst	Unleaded	EPA	30 mph steady state 60 mph steady state Cold start test	About 0.01 - 0.02
		Ford	60 mph steady state	0.01
Noble metal monolith catalyst	Unleaded	EPA	30 mph steady state 60 mph steady state Cold start test	About 0.03 - 0.08
		Ford	60 mph steady state	0.12
Base metal pelleted catalyst	Unleaded	EPA	30 mph steady state 60 mph steady state Cold start test	About 0.02 - 0.05

SO₂ by similar reactions. This storage and release makes the previous driving history of a catalyst vehicle very important. For example, sulfate emissions obtained over the FTP from a vehicle previously operated at low speed conditions may be somewhat higher than those on an FTP preceded by high speed conditions. Also, it is possible that sulfate would be stored during an FTP to be released later under high speed driving conditions. The work done over the past year has determined the magnitude of these factors to a preliminary extent.

The work done has used two basic sampling methods for automotive sulfate emissions, the condensation method using a dilution tunnel and the absorption method using an isopropyl alcohol SO₃ scrubber. Most investigators are using the condensation method.

The condensation method uses a dilution tunnel to mix the exhaust approximately 10 to 1 with fresh air. A large blower displaces a constant amount of gas mixture including both the entire exhaust volume and whatever volume of dilution air is required at any instant to hold the total amount of gas constant. The exhaust gas and dilution air are mixed in the dilution tunnel and a small isokinetic sample is withdrawn through a filter trapping the particulates in the exhaust stream. This method can be used with either a transient driving cycle such as the FTP or a steady state driving condition. The amount of sulfate collected on the filter is measured either by a wet chemistry technique or X-ray fluorescence spectroscopy. In this method, SO₂ must be measured independently.

The absorption method has been adapted from the Volume 36, 247, December 23, 1971, Federal Register which gives a recommended method for measuring SO₃ and sulfate emissions from stationary sources. This method involves passing a small portion (about 0.5 CFM) of undiluted exhaust gas through either a Greenburg Smith impinger or the smaller type impinger used in the MBTH aldehyde method. The impinger contains an 80 percent solution of isopropyl which absorbs both SO₃ and sulfuric acid emissions. The isopropyl alcohol inhibits oxidation of the SO₂ which passes through the impinger. A second impinger in series follows the first one and contains a hydrogen peroxide solution which oxidizes the SO₂ to SO₃ which is absorbed in the solution. This method can be used to measure both SO₃ and SO₂ simultaneously. Since undiluted exhaust gas is sampled, several sampling trains can be set up to simultaneously make measurements before and after the catalyst as well as at the tailpipe. Since this method takes a constant volume of undiluted exhaust regardless of the total exhaust flow (which varies greatly under different driving conditions), a sample proportional to the total exhaust can be taken only under steady state conditions. This method cannot accurately determine sulfate emissions over a transient driving cycle such as the FTP.

Theoretically, it would be possible to sample over a transient driving cycle with this method using exhaust diluted by a CVS type system. However, it is possible that the much lower level of H₂SO₄ in the diluted exhaust cannot be measured by this method.

General Motors, Ford, Ethyl, ORD, and OMSAPC have used the condensation method. Chrysler, OMSAPC, Ethyl, and, to some extent, GM have used the absorption method. Ford also has used the Goksoyr-Ross method for sulfate measurement which is described in Section 4.

Section 3 - General Motors Work on Sulfates

General Motors has done extensive studies in the sulfate area including work developing measurement procedures for sulfates and SO₂, developing emission characterization data for sulfates, and determining what factors affect sulfate emissions. These three areas are discussed in the following three subsections.

3.1 GM Work on Measurement Methods

The primary method used by GM to obtain sulfate emission data is the condensation method with a dilution tunnel. All of the GM data discussed in Section 3.2 was obtained by this method.

GM has run limited tests with the absorption method using the isopropyl alcohol bubblers. The initial tests run by GM on the catalyst vehicle GM loaned to EPA for testing involved a comparison of the condensation method with the absorption method. The absorption method showed substantial sulfates before the catalyst which indicates sulfates would also be found at these levels in non-catalyst systems. However, none of the GM work on non-catalyst cars discussed in Section 3.2 showed sulfates at this level from non-catalyst vehicles. Even the after catalyst numbers by both methods do not agree and show no clear trend. Table 2 summarizes these results.

TABLE 2
Comparison of Absorption and Condensation
Method for Sulfates

<u>Catalyst</u>	<u>Driving Cond.</u>	<u>Sulfate Emissions (gpm)</u>		
		<u>Condensation Method</u>	<u>Absorption Method</u>	
			<u>Before Cat.</u>	<u>After Cat.</u>
HN 2364	30 mph	0.013	0.009	0.018
	60 mph	0.029	0.019	0.016
	60 mph	0.039	0.006	0.025

However, after completing the above tests, GM ran additional tests on a non-catalyst car using the absorption method and found variable results. In one case, with technical grade isopropyl alcohol in the impingers, no sulfate emissions were found. In a second run when much purer reagent grade alcohol was used, significant sulfate was measured from the non-catalyst car. GM speculates that an impurity in the technical grade alcohol inhibited SO₂ oxidation so that the method gives the correct result.

GM now feels that the absorption measurement is a valid way to measure sulfates provided a second alcohol bubbler is used to check whether any SO₂ oxidation occurred. GM feels much additional development work should be done with the absorption method including cross checks between different laboratories.

Another method to measure sulfates has been developed by GM involving use of the TECO SO₂ instrument. First, the SO₂ content of the sample is measured. Then, a sample is passed through a quartz tube held at about 1000°C which causes thermal decomposition of sulfuric acid to SO₂. The SO₂ is measured again, which this time represents both the SO₂ and sulfate originally in the sample.

GM feels that this instrumental approach could possibly be developed to supplement or even replace the filter method. This analysis would be much simpler than the filter analysis and could conceivably be used to follow transients during a driving cycle.

3.2 GM Emission Data

GM has measured sulfate emissions from about six non-catalyst vehicles using the FTP or 60 mph steady state conditions. The results of these tests are in Table 3 and show little sulfate formation without a catalyst.

TABLE 3

GM Non-catalyst Vehicle Sulfate Data

<u>Vehicle</u>	<u>Fuel Sulfur Level</u>	<u>Test</u>	<u>Sulfates gpm</u>
1973 Chev.	0.02%	1972 FTP (8x)	<0.001
1973 Chev.	0.15%	1972 FTP	0.003
1973 Pontiac	0.04%	1972 FTP	0.001
1973 Chev.	0.02%	60 mph	<0.001
1973 Chev.	0.15%	60 mph	0.005

GM has also conducted extensive measurement of sulfate emissions on both monolith and pelleted catalysts over the FTP. Somewhat more limited tests were run under other conditions such as 60 mph and other speeds. GM measured sulfate emissions from catalysts with and without air injection and found much higher results with air injection. The results of the GM tests are given in Table 4. All of these measurements were taken with the GM dilution tunnel. All of the data in this table is taken from tests using 0.03% sulfur gasoline or from other tests normalized to a 0.03% sulfur level.

TABLE 4
GM Sulfate Emission Data

<u>Catalyst</u>	<u>Air</u>	<u>Driving Condition</u>	<u>Number of Tests</u>	<u>Average Sulfate¹ gm/mi</u>
Pelleted	Yes	1972 FTP	23	.0095
Monolith	Yes	1972 FTP	8	.0258
Pelleted	No	1972 FTP	6	.0018
Monolith	No	1972 FTP	2	.0012
Pelleted	Yes	60 mph ²	3	.0737
Pelleted Base Metal	Yes	60 mph ²	2	.0224
Pelleted	No	60 mph ²	1	.0127
Pelleted	Yes	60 mph ³	2	.0481
Monolith	Yes	30 mph ³	1	.0618
Monolith	Yes	40 mph ³	1	.0757
Monolith	Yes	60 mph ³	1	.0485
Pelleted	No	10 mph ³	1	.0000
Pelleted	No	30 mph ³	1	.0088
Pelleted	No	60 mph ³	3	.0438

1 This is an average (except for single test values) of the sulfate figures after having been linearly normalized to a fuel sulfur content of 0.03 wt.%.

2 Single test after FTP

3 Extended steady state tests

These results show the pelleted catalyst seems to have much lower sulfate emissions than the monolith catalyst over the FTP when both vehicles are equipped with air injection. Without air injection, both monolith and pelleted catalysts have even lower sulfate emissions. Interestingly, the limited number of tests taken show pelleted and monolith catalysts to have similar sulfate emissions without air injection even over the FTP. One other point to note is this preliminary work shows that HC and CO emissions seem to increase significantly without air injection as shown by the results in Table 5 for two similar cars with the same type of pelleted catalyst but with and without air injection.

TABLE 5
Effect of Air Injection on Gaseous Emissions

1975 FTP				
<u>Car</u>	<u>Air Injection</u>	<u>HC</u>	<u>CO</u>	<u>NOx gpm</u>
0-39680	Yes	0.35	4.45	2.06
0-38608	No	0.94	11.44	1.91

However, the GM data show the pelleted and monolith catalysts to have similar sulfate emissions at 60 mph. GM data also show the total amount of sulfur compounds (i.e., SO₂ and sulfates) emitted at 60 mph for the pelleted catalyst to be much greater than can be accounted for by the amount of sulfur in the fuel. The SO₂ readings were especially high. Apparently, sulfur compounds stored on the catalyst at lower speeds are emitted at higher speeds. The GM data indicate a large amount of SO₂ being released from the catalyst at 60 mph. Possibly, much of the stored sulfur is released as SO₂ rather than sulfates. However, more work is needed to determine the magnitude of sulfate emissions immediately after extended low speed operation.

Storage of sulfates on a catalyst is caused by a chemical reaction of these compounds with the alumina. Sulfates interact with the alumina to form sulfate salts. The large amount of alumina (6-7 pounds) in a pelleted catalyst can result in a high storage of sulfur compounds. Since there is insufficient alumina to store sulfates over the lifetime of the vehicle, the stored sulfates must be later released.

The storage would be much less with a monolith catalyst which consists of a lower mass cordierite support coated with alumina. While the sulfur compounds would react with the alumina to produce storage effects, it would not react with the cordierite support. The storage on the catalyst pellets is reversible at higher temperatures resulting in a decomposition of the aluminum sulfate salts.

GM measured sulfate emissions with fuels of various sulfur levels and found sulfate emissions are proportional to fuel sulfur levels. However, the test results do not necessarily show a linear relationship as was assumed in deriving the data in Table 4. This is in contrast to other test results such as Exxon's which show a linear relationship.

3.3 Factors Affecting Sulfate Emissions

GM has done some preliminary work to determine how the following parameters affect sulfate emissions:

- Catalyst formulation
- Catalyst temperature
- Air injection rate
- Space velocity

Regarding catalyst formulation, GM feels a pelleted catalyst emits less sulfate than a monolith catalyst. This is true under FTP conditions where large amounts of sulfates are stored on the pelleted catalyst. However, sulfate emissions are equivalent from the two different types of catalysts at 50 mph.

GM determined that noble metal loading has only a small effect on sulfate emissions. A laboratory apparatus with engine exhaust and catalysts containing 0.1% and 1.0% platinum were used for these tests.

Theoretically, catalyst temperature is expected to have a significant effect on sulfate formation. The thermodynamic equilibrium constant for SO_2 oxidation is such that higher temperatures lead to decreased sulfate formation. However, if the reaction activation energy is sufficiently high, a certain temperature is required to obtain a sizeable reaction rate. Thus, at lower temperatures, the SO_2 oxidation reaction would be very slow and at higher temperatures SO_2 will not oxidize. Catalysts operate most of the time in the temperature range where SO_2 oxidizes readily. Low temperature operation is not feasible because HC and CO oxidation is also very slow. High temperature operation results in poor durability.

GM did several experiments measuring SO_2 oxidation rates on pelleted catalysts at various temperatures. These test results indicate that increasing the catalyst temperature to 1200°F results in a slight increase in sulfate emissions beyond which sulfate emissions decrease. However, SO_2 emissions increase greatly with increasing temperature. These tests suggest that modifying catalyst temperature is not an effective control technique. Additional work is necessary, including work with other catalysts and vehicle tests, to confirm this preliminary conclusion.

One item of interest noted in these tests was that emissions of SO_2 and sulfates combined were less than the sulfur input into the catalyst at lower temperatures but increased with increasing temperatures. This is due to storage of sulfur compounds on the pelleted catalyst at lower temperatures which are released at higher temperatures. As the temperature increases, the percentage of total sulfur compounds represented by sulfates decreases. More work is needed to determine quantities of sulfur compounds released from a pelleted catalyst at various temperatures.

Air injection rate is expected to affect sulfate formation in that excess oxygen results in higher sulfate formation with all other conditions (e.g., catalyst temperature) being identical. Initial work in this area was done by GM who measured sulfate emissions of catalyst cars with air pumps and without air pumps. Substantial increases in sulfate emissions were found in this preliminary work for both pelleted and monolith catalysts with use of air pumps.

GM did some additional tests measuring the effect of two levels of oxygen on sulfate formation at five different temperatures. These results, given in Table 6, show that a two-fold increase in oxygen level approximately doubles the amount of sulfate found.

TABLE 6

Effect of Oxygen Level on Sulfate Formation

<u>Catalyst</u>	<u>%O₂</u>	<u>SO₃ (ppm)</u>				
		<u>900°F</u>	<u>1000°F</u>	<u>1100°F</u>	<u>1200°F</u>	<u>1300°F</u>
0.1% Pt. (A/F 15.4, SV 28,000)	1%	5.0	4.5	-	7.2	6.5
0.1% Pt. (A/F 16.2, SV 17,500)	2%	12.7	10.7	11.8	-	-

While these results show the effect of oxygen level on sulfate emissions, they indicate no clear trend of catalyst temperature versus sulfates. This is contrary to the earlier findings of sulfate emissions increasing with increasing temperature up to 1200°F beyond which they decrease. However, these results are very promising in that they indicate a large reduction of sulfates with lower oxygen levels. Close control of air injection rate could be a promising way to control sulfate emissions and should be investigated further.

Space velocity is, in effect, the total time period in which the exhaust gas is in contact with the catalyst. It is expressed in bed volumes per hour which indicate the total number of catalyst beds of a given volume the exhaust gas could pass through in an hour. A smaller catalyst bed results in a higher space velocity number. A larger catalyst bed generally results in more effective HC and CO oxidation and is less likely to suffer "break through", that is, unreacted exhaust gas passing through if the bed is too small. However, a catalyst bed that is too large (i.e., a low space velocity number) will have a very long warm-up period and high cold start emissions. A trade-off is made between these two factors to define an optimum space velocity. Sulfate emissions can also be affected by space velocity with a low space velocity resulting in higher sulfate emissions. It should be possible to add sulfates as another variable in defining optimum catalyst space velocity.

GM is the only company to date running tests to determine the effect of space velocity on sulfate formation. These tests are summarized in Table 7 and were run at 1200°F with a pelleted catalyst.

TABLE 7
Effect of Space Velocity on Sulfate Formation

<u>Space Velocity</u>	<u>Sulfate Formation</u>
7,000 hr ⁻¹	18%
28,000 hr ⁻¹	14%

These test results show greater sulfate emissions at the lower space velocity which allows more time for the sulfate to form in the catalyst. This result suggests that sulfate formation is limited by reaction kinetics (i.e., reaction rates) rather than thermodynamics. Even though the effect of space velocity is relatively small, it is, nevertheless, one more variable to consider in designing a catalyst for low sulfate emissions.

These test results are very encouraging in that they indicate several parameters which affect sulfate emissions. It is possible that a catalyst could be designed for low sulfate emissions and still meet HC and CO standards.

Section 4 - Ford Motor Company Work on Sulfates

Ford analyzed the samples collected under the EPA contract with Dow, in which sulfuric acid emissions were first found from catalyst vehicles. Ford is currently exploring this problem by the following three phase program:

- Phase 1 - This involves engine dynamometer testing at steady state speeds to develop sampling and analysis methodology. Both sulfate and SO₂ emissions are being analyzed as discussed later.
- Phase 2 - Emission data for sulfates and SO₂ will be obtained from vehicles using the 1975 FTP.
- Phase 3 - The effects of parameters such as catalyst type and age, temperature, oxygen level, and space velocity on sulfate emissions will be determined. The mechanism of any sulfate storage phenomenon will be investigated.

Ford has completed the first phase of this project by a contract with Battelle Laboratories. Ford will start the second phase of this project in-house later this year. Ford has already started the third phase of their project using a small laboratory rig to simulate vehicle conditions.

Ford measured sulfate emissions in the first phase of their program by the following two methods:

- (1) the dilution tunnel method using filters to collect sulfates from a small stream of diluted exhaust.
- (2) the Goksoyr-Ross method using a condensation coil to condense sulfates from a small stream of undiluted exhaust.

The condensation or dilution tunnel method is being used by other investigators. Ford is the only investigator using the Goksoyr-Ross method which involves condensing sulfuric acid from a small stream of undiluted exhaust. The acid is condensed in a glass coil at 60-90°C and measured by the gravimetric method. The SO₂ passes through the coil uncondensed and is removed by a hydrogen peroxide solution. The SO₂ sample collection and analysis is identical to that in the absorption method described in Section 2. The Goksoyr-Ross method, like the absorption method, can only be used for steady state conditions when concentrated exhaust is used.

The tests under phase 1 were run on an engine dynamometer at Battelle and are summarized in Table 8.

TABLE 8
Ford Sulfate Emission Data

<u>Catalyst Type</u>	<u>Speed mph</u>	<u>Number of Tests</u>	<u>Average H₂SO₄ gpm[*]</u>
None	60	5	0.0011
Monolith	60	8	0.057
AC Pelleted	60	2	0.051
AC Pelleted	30	2	0.074

* H₂SO₄ figures have been normalized to .03 wt.% Sulfur fuel before averaging.

Ford measured SO₂ in all of these tests to obtain a sulfur balance. Ford also measured both SO₂ and sulfates at several places along the exhaust system including both upstream and downstream of any catalyst present. Ford ran tests only at 60 mph since they wanted to develop the measurement methodology before obtaining emission data under other test conditions. The Ford data at 60 mph are in excellent agreement with the GM and Exxon data at 60 mph.

The tests on the engine without a catalyst showed only very small amounts of sulfate with almost all of the fuel sulfur recovered as SO₂. Furthermore, Ford obtained an excellent material balance upstream of the catalyst finding almost all of the fuel sulfur as SO₂ before the catalyst. These results strongly indicate that very little sulfate is formed without a catalyst.

Ford did extensive tests on monolith catalysts at 60 mph and more limited tests on pelleted catalysts at 30 and 60 mph. Ford finds almost no storage of sulfates on the monolith catalyst at 60 mph. However, Ford finds significant storage of sulfates with the pelleted catalysts at both speeds, especially when the catalysts are fresh. The magnitude of the storage effect is shown in Table 9.

TABLE 9
Ford Sulfur Balances

Type of Catalyst	Speed mph	Total Particulate* gpm	Sulfur Compounds		
			SO ₃ , SO ₄	SO ₂	Lost in System
Monolith	60	0.14	38±9%	53±5%	11±7%
					<u>Stored in Catalyst</u>
Pelleted, new	60	0.10	28%	40%	32%
Pelleted, after 1300 mi.	60	0.12	34%	40%	25%
Pelleted, "new", after the above 60 mph	30	0.11	31%	6%	63%
Pelleted, after 1120 mi. at 30 mph	30	0.29	68%	12%	23%

* Particulate normalized linearly to .03 wt.% sulfur fuel.

No data are available yet from the third phase of the Ford program. A laboratory rig with a small catalyst sample and synthetic exhaust gas is being used for this study. Conditions such as catalyst formulation, catalyst temperature, air injection rate, and catalyst residence time are being varied to determine their effect on sulfate emissions.

Section 5 - Chrysler Corporation Work

Chrysler Corporation has done extensive measurement of sulfate emissions from both catalyst and non-catalyst cars using the absorption method. Chrysler has also done considerable work to evaluate use of this method. Both areas will be discussed in the following sections.

5.1 Chrysler Work on Method Development

Chrysler has used the absorption method for the work discussed in Section 5.2. This method involves bubbling a small portion of undiluted exhaust directly into a small impinger, the same type used in the MBTH aldehyde measurement method, filled with an 80 percent solution of isopropyl alcohol. The SO_3 and sulfates are measured by titration. Chrysler measured the SO_2 directly with a DuPont Model 411 SO_2 analyzer. Chrysler did all of its measurements using a hot start 1975 FTP. As mentioned in Section 2, it is not valid to use this type of sampling system, which takes a small sample of undiluted exhaust at a constant flow rate, in a transient driving cycle. A transient driving cycle gives various exhaust flow rates which would result in a sample not proportional to the actual emissions. However, Chrysler feels this sampling system is valid for indicating trends in sulfate emissions. Chrysler feels it may be valid to take SO_3 samples directly from a bag using the standard CVS-FTP test. Chrysler took SO_3 bag samples from two cars using the absorption method. The numbers compared well with those obtained from cars sampling concentrated exhaust over the FTP with the absorption method. However, the SO_3 (or sulfate) could be partially lost by condensation on the walls of the bag which would introduce an error into this method. Even though these results are encouraging much more work is needed to justify use of the absorption method for bag samples. Comparisons with the condensation method by different companies are needed.

Chrysler did extensive work to evaluate the validity of the absorption method. The initial work was done in a tube furnace containing catalyst samples and showed substantial formation of SO_3 over a catalyst. Samples of SO_2 and O_2 passed through the empty tube furnace at 1000°F showed no sulfate being formed. However, exhaust components such as nitrogen oxides may affect SO_2 oxidation in the sampling systems. Chrysler passed a mixture of SO_2 , O_2 , H_2O , NO , and CO through the empty tube furnace at 1100° and other temperatures to address this point and found no SO_3 .

In addition to the tube furnace work, Chrysler has done additional tests with a single cylinder engine to justify the method. An engine test was run with isooctane fuel containing no sulfur to see if non-sulfur exhaust components will give a positive SO_3 reading. Again, no SO_3 response was noted. Chrysler then introduced some SO_2 into the exhaust system with the engine presumably operating on isooctane fuel which would check whether other exhaust components result in SO_3 formation. About five percent of the SO_2 was converted to SO_3 , as reported to EPA on October 12, 1973, indicating formation of SO_3 in either the exhaust or sampling system. Chrysler

reported another test where SO_2 and nitrogen were introduced into the exhaust system of the engine running on isooctane fuel. No SO_3 was found in this test probably because of the lower oxygen levels than in the preceding test. However, Chrysler reported another test to EPA on November 2, 1973, in which SO_2 was introduced into the exhaust system of the engine running on isooctane fuel with no SO_3 being found.

Chrysler also did an experiment introducing SO_2 into the sample probe which was at full operating temperature with the engine running on isooctane fuel. No SO_3 was found. Chrysler then introduced SO_2 into the impinger itself with the engine running on isooctane fuel and found no SO_3 . Chrysler did a third experiment adding particles from the exhaust systems, presumably iron type compounds, and titrating the impinger solution without any exhaust being passed through the system. The titration showed no SO_3 to be present demonstrating the exhaust particles by themselves do not give a positive SO_3 reading. Chrysler then ran a sample of engine exhaust from a sulfur containing fuel through the impinger system with exhaust system particles in the impinger. The amount of SO_3 was 60 percent less than that found without the exhaust system particles in the impinger. This indicates the exhaust system particles somehow react with the SO_3 , possibly by adsorption.

Chrysler has run several single cylinder engine tests with a catalyst in the system and, in all cases, found increased SO_3 formation over the catalyst. These tests Chrysler ran involved measuring sulfate emissions from CVS bags identical to those used for HC, CO, and NO_x emissions. This involves dilution of the exhaust by a CVS type system which is the first time the absorption method has been used for dilute exhaust. In one of these tests with 0.4 percent sulfur fuel, 120 parts per million (ppm) and 240 ppm of SO_3 were found before and after the catalyst respectively. Another single cylinder engine test using 0.4 percent sulfur fuel, which would give 265 ppm of SO_2 if no SO_3 was present, showed 63 ppm SO_3 before the catalyst and 77 ppm SO_3 after the catalyst.

5.2 Chrysler Vehicle Tests

Chrysler has conducted extensive vehicle tests using the absorption method over a hot start 1975 FTP type test. As mentioned in Section 5.1, the emission numbers were obtained using the absorption method over a transient driving cycle and are not accurate emission numbers.

Chrysler has tested a large number of non-catalyst cars and, contrary to the results of other investigators, reported in Sections 3 and 4, has found substantial sulfate emissions. Six 1975 non-catalyst prototypes, two with air pumps and four running lean, were tested with both leaded and unleaded fuel. One 1973 production car was tested with leaded and unleaded fuel. The sulfate emission results and percent sulfate formed are listed in Table 10.

TABLE 10

Non-catalyst Sulfate Vehicle Emission Data
from Chrysler Modified 1975 FTP

<u>Vehicle</u>	<u>Fuel Sulfur Level Percent</u>	<u>Lead Level g/gal</u>	<u>H₂SO₄ Emissions gpm</u>	<u>Percent S Converted to H₂SO₄</u>
Car 185, 1975 Prototype				
air pump on	0.1	0	0.13	16
air pump off	0.1	0	0.20	18
air pump on	0.012	3.2	0.009	9
Car 294, 1974 Production	0.014	0	0.013	17
Car 394, 1975 Prototype (lean)	0.1	0	0.15	15
Car 588, 1975 Prototype (lean)	0.034	2.2	0.016	6
Car 403, 1975 Prototype (air pump)	0.014	0	0.031	25
Car 775, 1975 Prototype (Ethyl lean reactor)	0.1	0	0.14	16
Car 612, 1973 Production car (no air pump)	0.014 0.027	0 1.6	0.017 0.01	14 5
Car 032, Honda CVCC	0.012	3.2	0.006	6

These results show slightly less than 20 percent conversion to sulfate for non-catalyst cars using unleaded fuel. Less than 10 percent conversion to sulfates occurs when leaded fuel is used. Leaded fuel results in the formation of some lead sulfate which may not be measured by the absorption method due to its slow solubility. The lead sulfates may also be stored temporarily in the exhaust muffler. However, it is significant that leaded fuel showed lower sulfate emissions than unleaded fuel. These results have not been confirmed by other investigators.

The percentage of fuel sulfur converted to sulfate was usually determined by the amount of SO_3 and SO_2 found in the exhaust rather than comparing the amount of SO_3 with the amount of fuel sulfur. Frequently, the total amount of sulfur recovered was greater than the amount theoretically burned in the engine. This is the reason why SO_3 emissions can be substantially higher in one case (e.g., Car 185 with the air pump on versus air pump off) with no change in percent sulfates and SO_2 . A large part of this problem is probably due to the sampling method used. It is also conceivable that sulfates (e.g., iron sulfates) could be stored in the muffler in one driving condition and emitted in another. At any rate, much more work is needed on the sulfur balance to make firm conclusions.

Chrysler has also measured sulfate emissions from a number of vehicles with pelleted and monolithic oxidation catalysts. The results of these tests are given in Table 11.

TABLE 11
Catalyst Sulfate Emission Data from Chrysler
Modified 1975 FTP

<u>Vehicle</u>	<u>Fuel Sulfur Percent</u>	<u>H₂SO₄ Emis- sions gpm</u>	<u>Percent S Con- verted to H₂SO₄</u>
Car 411, 1975 Monolith Catalyst (0 miles)			
Before catalyst	0.1	0.20	23
After catalyst	0.1	0.29	34
Car 554, 1975 Pelleted Catalyst			
0 miles	0.014	0	0
200 miles	0.014	0.017	13
400 miles	0.014	0.023	19
20,000 miles (4 different catalysts)	0.014	0.012	10
Car 554, Monolithic Catalyst			
0 miles	0.014	0.010	9
200 miles	0.014	0.010	8
2,000 miles	0.014	0.012	10
50,000 miles	0.1	0.009	10

These results show that a catalyst causes increased SO_2 oxidation but a significant amount of SO_3 exists before the catalyst. The Chrysler tests are the only tests other than the OMSAPC tests of EPA which show a significant amount of sulfate from non-catalyst vehicles. More work is clearly needed to determine if this is an actual phenomenon or caused by errors in the measurement method.

5.3 Chrysler Tests of Catalyst Poisoning

Some very recent work has been done by Chrysler on lead poisoning of catalysts. This work was reported by Dr. Maxwell Teague of Chrysler on April 14, 1974 at an EPA sponsored symposium titled, "Health Consequences of Environmental Controls: Impact of Mobile Emissions Controls". The paper by Dr. Teague was titled, " SO_4 Emissions From Oxidation and Non-oxidation Catalyst-Equipped Vehicles" and discussed, for the most part, the sulfate emission data given in the OMSAPC progress report.

However, Chrysler also reported some engine dynamometer tests run with various combinations of lead, ethylene dibromide, and ethylene dichloride in gasoline. Ethylene dibromide and ethylene dichloride are added with tetraethyl lead (or other alkyl lead compounds) to serve as scavengers insuring that lead is removed from the combustion chamber as the volatile lead chloride or bromide type compounds. Chrysler ran tests with gasoline containing the following additive combinations:

- (1) lead additive (3 g/gal) with both ethylene dibromide and ethylene dichloride
- (2) ethylene dibromide and ethylene dichloride without lead additive
- (3) lead additive by itself with no scavengers
- (4) lead additive (2 g/gal) with ethylene dichloride only.

For each of the above four combinations, the catalyst conversion efficiency on an engine dynamometer for HC and CO was monitored. A serious decrease in catalyst efficiency was noted for the first two additive combinations, (1) and (2). However, no significant change in catalyst efficiency occurred for the last two packages.

This preliminary work indicates that ethylene dibromide poisons catalysts while lead itself and ethylene dichloride have little poisoning effect. Chrysler feels it may be possible to run catalyst equipped vehicles with leaded fuel, provided no ethylene dibromide is used. Furthermore, the presence of lead could perhaps lower sulfate emissions. Chrysler is continuing tests to see if engine and catalyst durability are satisfactory for leaded fuel with ethylene dichloride scavenger. It is possible that both ethylene dichloride and ethylene dibromide scavengers are required when lead is used for satisfactory engine durability.

The EPA Office of Mobile Source Air Pollution Control on May 2, 1974 requested from Chrysler complete details of their tests and also requested the comments of a few other automobile manufacturers, catalyst manufacturers, gasoline additive manufacturers, and petroleum companies on these points.

The responses to EPA have been analyzed. The primary conclusion made is that leaded gasoline as it is currently formulated with both scavengers will poison catalysts. Whether an engine can operate satisfactorily and avoid valve problem on gasoline with lead only or lead and ethylene chloride has not been established. Furthermore, the data from Ford, GM, and Exxon indicate that lead by itself poisons catalysts. The contradictory data on catalyst poisoning has yet to be resolved. Additional data are still required to assess whether operation of catalyst vehicles on fuel with lead alone or lead and ethylene dichloride is feasible.

Section 6.1 - Exxon Research and Engineering Work

Exxon Research and Engineering has done extensive work on measuring sulfate emissions from catalyst and non-catalyst vehicles. Exxon has also done considerable work developing sampling procedures for particulates and sulfates.

Exxon uses the condensation method with a dilution tunnel to measure sulfates and has not used the absorption method. The Exxon dilution tunnel has provisions to dehumidify and chill the incoming dilution air and can take filter samples at lower temperatures (90°F) without water condensation which usually occurs at these temperatures. While the Exxon dilution tunnel is smaller in diameter than the one used by EPA, GM, and Battelle, it should be just as effective for sulfate collection.

Exxon tested monolith catalyst, pelleted catalysts and non-catalyst vehicles at 40 mph, 60 mph, and over the FTP. A summary of the Exxon results is given in Table 12.

TABLE 12

Exxon Research and Engineering Sulfate Emission Data

<u>Catalyst</u>	<u>Driving Condition</u>	<u>Number of Tests</u>	<u>Average Sulfates gpm</u> ¹
Monolith	1972 FTP	18	0.066
Monolith	40 mph Cruise	18	0.048
Monolith	60 mph Cruise	4	0.053
Pelleted	1975 FTP	13	0.017
Pelleted	40 mph Cruise	4	0.015
Pelleted	60 mph Cruise	22	0.060
None	1972 FTP	1	0.005
None	40 mph Cruise	4	0.0004

¹ These are averages of the sulfate figures after they have been linearly normalized to a fuel sulfur content of 0.03 wt.%.

These data show significantly greater sulfate emissions from the monolithic catalysts than from the pelleted catalysts under FTP and 40 mph conditions. However, both catalysts have similar sulfate emissions at 60 mph. For the monolith catalyst, this is equivalent to a 25-35% conversion of the fuel sulfur to sulfate at 40 or 60 mph as well as the FTP. For the pelleted catalyst, this is equivalent to 5-10% over the FTP or 40 mph conditions. At 60 mph, this is equivalent to a 25-35% conversion for the pelleted catalyst. In all cases, the sulfate emissions were proportional to fuel sulfur content.

These results agree with the GM results which show that the pelleted catalyst stores sulfates at lower speeds where the catalyst temperature is lower. However, this phenomenon is reversible and sulfur compounds are released at higher temperatures which occur with higher speeds. It is important to measure the amount of SO_2 from catalyst cars to determine a sulfur balance and the form in which these compounds are released.

Exxon also tested several non-catalyst vehicles for sulfate and SO_2 emissions. Exxon had difficulty measuring the low sulfate emissions over the FTP but was able to obtain an accurate emission figure over an extended 40 mph cruise. The sulfate emissions at 40 mph were 0.004 gpm or 0.5% of the fuel sulfur with the remaining fuel sulfur being converted to SO_2 .

Section 7 - Ethyl Corporation Work

Most of the Ethyl Corporation work has been on measurement methodology with some limited work on obtaining emission factors on catalyst and non-catalyst cars.

7.1 Ethyl Method Evaluation Work

Ethyl initially evaluated the absorption method by passing mixtures of SO_2 through the impingers to see if any sulfate readings were obtained from SO_2 oxidation in the impingers. Ethyl found a significant amount of SO_2 trapped in the first impinger and measured as sulfate.

Ethyl feels this error is less when the first impinger contains sulfuric acid which suppresses the solubility and oxidation of SO_2 . This error would be less for catalyst cars which emit sulfuric acid which is trapped by the first impinger. Ethyl states that a spuriously high sulfate reading would be found from non-catalyst cars. For catalyst cars, the error would be smaller.

Ethyl tested this hypothesis through a modification of Method 8 by adding a known amount of sulfuric acid to the first impinger. The amount of sulfate found from non-catalyst cars was lower than found previously. Ethyl states this modification lowers but does not eliminate the error due to SO_2 oxidation.

Ethyl also measures sulfate emissions by a modified condensation method. This method does not involve a dilution tunnel but rather uses a large black bag (100 m³ volume) which holds the entire vehicle exhaust from a test cycle and sufficient dilution air to allow cooling and condensation of exhaust particulates. Ethyl has used this system in the past to measure total particulate, lead, and POM emissions. Ethyl finds that sulfates are lost to the walls of the bag over extended time periods. Even though the exhaust is in the dilution tunnel for only several seconds in the GM, Exxon, and EPA methods, work should be done to insure no losses occur in the dilution tunnel. Ethyl is still developing and validating their air dilution method.

Ethyl included in their submission complete analytical details for their analysis techniques which are helpful to EPA and other investigators. Ethyl uses an iodine method to analyze the sulfates collected. They use the West-Gaeke method to analyze SO₂ and obtain a sulfur balance.

7.2 Ethyl Vehicle Sulfate Data

Ethyl has obtained sulfate emissions from only a limited number of cars. These cars include the following three non-catalyst cars and one catalyst car:

- 1973 Chevelle, production car
- Ethyl lean reactor car
- Pinto with rich reactor system
- 1973 Chevelle with Engelhard catalyst.

Only trace quantities (less than 1%) of sulfate were found with the 1973 production car. No sulfate was detected for the two thermal reactor cars. Ethyl also measured SO₂ and obtained good sulfur balances for the 1973 production car and the rich reactor car. However, only 50% of the fuel sulfur was recovered in the black bag for the lean reactor car showing work is still needed to develop measurement methodology.

For the catalyst car, six tests were made on the low mileage catalyst. At 40 mph steady state, Ethyl found about 0.07 gpm of sulfates which is higher than the Exxon value of 0.05 gpm for 40 mph cruise. Ethyl noted only a 50-60% recovery of total sulfur and is doing further work on this.

Section 8 - EPA OMSAPC Test Results

8.1 Introduction

Both the OMSAPC and ORD have done extensive work measuring sulfate emissions. The OMSAPC in-house work has measured sulfate emissions on the following five vehicles using the absorption method:

- Ford - Engelhard Catalyst
- 1975 GM Non-catalyst Prototype
- 1975 GM Catalyst Prototype
- Gould Dual Catalyst Vehicle
- Opel Diesel

OMSAPC also has a dilution tunnel installed and has taken particulate and sulfate with the condensation method on the following cars:

GM Catalyst Prototype
Ford Catalyst Prototypes
Gould Dual Catalyst Vehicles
Peugeot Diesel
Mercedes Diesel

Honda CVCC
Ford Stratified Charge
Volvo Three Way catalyst
Ford Non-catalyst
Dresser Carburetor Prototype

In addition to this work, OMSAPC has funded a contract effort at Dow to measure catalyst particulates. The OMSAPC Dow contract has measured sulfate emissions on the following five vehicles:

Ford-Engelhard Catalysts (same vehicle tested
by OMSAPC in-house)
Peugeot Diesel
Mazda Rotary
Williams Gas Turbine
GM Catalyst Vehicle

The OMSAPC results are covered in this paper while the ORD results are covered in a parallel paper. Both OMSAPC and ORD have planned extensive additional work in this area.

8.2 EPA-OMSAPC Work With Absorption Method

OMSAPC has obtained extensive emission data with the absorption method described in Section 2. This method involves sampling a small portion of undiluted exhaust with a quartz probe. The exhaust is bubbled through three impingers in series containing an isopropyl alcohol in the first impinger to absorb SO_3 and sulfates and a hydrogen peroxide solution in the second and third impingers to absorb SO_2 .

These tests were run at three steady state speeds, 10, 30, and 60 mph using undiluted exhaust.

Of the five cars tested by this method, three vehicles were tested extensively. These three cars, which are conventional engine 1975 prototypes, are listed below:

- (1) 1975 Ford Prototype, air injection, quick-heat intake manifold, Engelhard catalysts (2 sets)
- (2) 1975 GM non-catalyst prototype, exhaust manifold air injection
- (3) 1975 GM catalyst prototype, 0-mile noble metal pelleted oxidation catalyst (0.05 oz. noble metal), no air injection.

The Ford vehicle was tested separately with two sets of Engelhard catalysts. One set had been run 50,000 miles while the second set had less than 500 miles. This vehicle was also tested without a catalyst. Limited tests were done on the following two additional cars:

- (1) Gould dual catalyst car, Gould Monel reduction catalyst and noble metal pelleted oxidation catalyst (0 miles on reduction catalyst, 12,000 miles on oxidation catalyst)
- (2) Opel Diesel

All of the OMSAPC tests have several limitations which must be noted. The reproducibility from test to test was very poor. While multiple tests were used to obtain average emission values, the reasons for the poor reproducibility should be understood so this problem can be corrected. The analytical method does not recover all of the sulfur compounds since the material balance is less than 100 percent. The material balance is poorer for the catalyst vehicles than for the non-catalyst vehicles but is variable for all vehicles. Clearly, much more work is needed to validate this method for mobile sources as it has been validated for stationary sources. Also, work is needed to compare emission results from this method to those obtained by the condensation method. Nevertheless, these test results do give a preliminary estimate of the problem. The values reported in this section are average values from many repeat tests.

The Ford vehicle was tested with high and low sulfur level fuel containing 0.085% and 0.017% sulfur respectively. The test results were interpolated to give an emission estimate for a 0.03% sulfur fuel assuming a linear relationship between fuel sulfur level and sulfate emissions.

Table 13 gives the results of the Ford tests for the vehicle in the following three configurations:

No catalyst
Fresh catalyst
50,000 mile catalyst

The percent conversion to sulfate was based on the ratio of sulfate and SO₂ found in the test. The percent sulfur recovered was based on comparing the SO₂ and sulfate found with the sulfur consumed by the engine.

The tests on the Ford vehicle showed the following:

- (1) There appears to be significant formation of sulfates (over 10 percent of the fuel sulfur is converted to sulfates) without a catalyst. These results are possibly due to errors in the measurement method.

TABLE 13

EPA Test on 1975 GM Prototype Non-catalyst Vehicle
Air Pump Disconnected

<u>Probe Location</u>	<u>Speed</u>	<u>Sulfates gpm</u>	<u>SO₂ gpm</u>	<u>% Conversion to Sulfate</u>	<u>% Sulfur Recovered</u>
Before muffler	10	0.09	0.15	27	86
	30	0.01	0.05	14	78
	60	0.02	0.11	8	104
At Tailpipe	10	0.03	0.17	12	79
	30	0.01	0.04	11	68
	60	0.008	0.09	5	80

- (2) A catalyst significantly increases sulfate formation (about 20-80 percent of the sulfur recovered was sulfates).
- (3) The amount of sulfate formed is about twice as great with a fresh catalyst as with an aged catalyst (50,000 miles).
- (4) Sulfate emission values are a maximum at 10 mph and a minimum at 60 mph steady state speeds. This could possibly be due to the lower catalyst temperature (750°F) at 10 mph versus 60 mph (1050°). The equilibrium conversion to sulfate decreases at higher temperatures.

The tests on the GM vehicles were more extensive than the Ford tests. Sulfate emissions were usually sampled at the following three locations:

- (1) Behind the exhaust manifold before any catalysts present
- (2) Immediately behind the catalyst in the exhaust system (or behind the reduction catalyst in a dual catalyst system).
- (3) At the tailpipe.

Tests were made on a 1975 non-catalyst prototype with the air pump operating and with the air pump disconnected. Tests were also made with a 1975 catalyst prototype with a fresh pelleted noble metal catalyst in the underfloor converter. This vehicle did not have an air pump. The GM test results are given in Tables 14, 15, and 16. Fuel containing 0.03% sulfur was used in these tests.

The following conclusions can be made from these tests:

- (1) Significant sulfate emissions were again found in the non-catalyst vehicle. This finding may well be a result of the measurement method rather than an actual phenomenon.
- (2) The sulfate emissions were slightly higher in the non-catalyst car with the air pump running than with the air pump disconnected.
- (3) Sulfate emissions with the catalyst car were significantly higher than for the non-catalyst car with much of the sulfate being formed over the catalyst itself.
- (4) Sulfate emissions were higher at 10 mph than at 30 mph. This could possibly be due to the lower catalyst temperature at 10 mph (750° at 10 mph versus 770°F at 30 mph).
- (5) Sulfate emissions are very high at 60 mph and are somewhat greater than at 10 mph. This would not be predicted from thermodynamic considerations since the high catalyst temperature at 60 mph (1120°F)

TABLE 14

EPA Test on 1975 GM Prototype Non-catalyst Vehicle
Air Pump Connected

<u>Probe Location</u>	<u>Speed</u>	<u>Sulfates gpm</u>	<u>SO₂ gpm</u>	<u>% Conversion to Sulfate</u>	<u>% Sulfur Recovered</u>
Before muffler	10	0.06	0.14	22	78
	30	0.008	0.04	11	65
	60	0.02	0.09	10	84
At tailpipe	10	0.02	0.15	8	71
	30	0.006	0.04	8	60
	60	0.009	0.09	5	82

TABLE 15
EPA Test on 1975 GM Prototype Non-catalyst Vehicle
Air Pump Disconnected

<u>Probe Location</u>	<u>Speed</u>	<u>Sulfates gpm</u>	<u>SO₂ gpm</u>	<u>% Conversion to Sulfate</u>	<u>% Sulfur Recovered</u>
Before muffler	10	0.09	0.15	27	86
	30	0.01	0.05	14	78
	60	0.02	0.11	8	104
At tailpipe	10	0.03	0.17	12	79
	30	0.01	0.04	11	68
	60	0.008	0.09	5	-80

TABLE 16

EPA Tests on 1975 GM Catalyst Prototype

<u>Speed</u>	<u>Probe Location</u>	<u>Sulfates gpm</u>	<u>SO₂ gpm</u>	<u>% Conversion to Sulfates</u>	<u>% Sulfur Recovered</u>
10	Before catalyst	0.03	0.15	12	97
	After catalyst	0.07	0.009	84	29
	At tailpipe	0.07	0.04	52	48
30	Before catalyst	0.009	0.05	8	77
	After catalyst	0.04	0.02	63	46
	At tailpipe	0.04	0.01	65	40
60	Before catalyst	0.02	0.10	10	101
	After catalyst	0.10	0.06	51	112
	At tailpipe	0.08	0.06	43	100

should result in lower sulfate formation. However, the pelleted catalyst may be storing sulfates formed at lower speeds and releasing them at higher speeds with the higher temperatures. The pelleted catalyst, with the large amount of alumina substrate, probably has a much greater tendency to store sulfates at lower temperatures. This storage results from chemical interaction with the substrate forming sulfate salts which are decomposed at higher temperatures. Such storage has been found occurring with pelleted catalysts from tests run by Exxon Research and Engineering

The test on the Gould dual catalyst car is the first sulfate test reported on a car equipped with a nitrogen oxide reduction catalyst. Duplicate tests were run at 10 and 30 mph. The tests showed some sulfate formation (16 percent and 30 percent for 10 and 30 mph, respectively) in the engine and exhaust manifold. The sulfate conversion, defined as percentage of the SO₂ and sulfates recovered as sulfates, increased to 50-60 percent after the reduction catalyst. The sulfate formation was higher yet (78 percent and 93 percent at 10 and 30 mph, respectively) at the tailpipe suggesting additional sulfates were formed in the oxidation catalyst and/or exhaust system. The overall sulfate emissions were about the same levels as those of the GM catalysts.

The Opel Diesel vehicle tested had a very small amount of the fuel sulfur (less than 5 percent) converted to sulfates in the limited tests at 60 mph done by OMSAPC. Even with the sulfur content of Diesel fuel being about ten times greater than gasoline, the sulfate emissions are about the same as from a spark ignition engine. However, the SO₂ emissions are much greater than from a conventional engine.

8.3 OMSAPC Work with Condensation Method

In-House Work

OMSAPC has measured sulfate and particulate emissions on twelve vehicles using a dilution tube to collect the samples and the chloranilate method to analyze them.

The dilution tube is 18 inches diameter and 22 ft. long. The sample point is 13 ft downstream of the point where the vehicle exhaust is introduced to the filtered air stream. The total flow rate through the tube is about 600 cfm. The samples are collected on a 47 mm diameter fluoropore filter using a sample flow rate of 2.2 cfm. The sample collection time period varies depending on the test condition and vehicle type.

The filter samples are weighed for total particulates using a Sartorius analytical balance and then analyzed for sulfates. The filters are dissolved in 65% isopropyl alcohol. A small amount of this liquid is pumped through a liquid chromatograph column (Varian

Model 8500) where the sulfate ions are quantitatively exchanged with chloranilate ions. The amount of chloranilate ion released is measured by ultraviolet spectroscopy (Varian Model 635). The system has recently become operational and data on ten vehicles are available. The analysis method has been found to be inappropriate for the diesel samples and must, therefore, be modified slightly before the stored diesel sulfate samples can be analyzed. However, the particulate weights have been determined and can be found in Table 22. Some of the diesel samples were analyzed by EPA-ORD and these preliminary results can be found in Tables 18 and 21.

The following twelve vehicles have been tested to date:

- | | |
|---|------------------------------------|
| 1) 1975 GM catalyst prototype | 7) Honda CVCC |
| 2) 1975 Ford catalyst prototype | 8) 1977 Ford Prototype |
| 3) Gould dual catalyst vehicle-25,000 miles | 9) Gould Dual Catalyst Veh.-0 mile |
| 4) Dresser carburetor vehicle | 10) 1974 Ford Production |
| 5) Peugeot Diesel | (non-catalyst) |
| 6) Mercedes Diesel | 11) Ford Stratified Charge |
| | 12) Volvo Three Way Catalyst |

Also, a Chrysler prototype catalyst vehicle was tested briefly but developed mechanical problems, was returned to Chrysler for repairs, and has been sent back to OMSAPC. In addition to these vehicles, the following vehicles are scheduled for testing in the near future.

GM Catalyst Prototype (designed to meet statutory HC and CO standard)
Texaco Stratified Charge
Non-catalyst 1975 vehicles
1975 Production Catalyst vehicles (GM, Ford, Chrysler)

An important car in this test program has been the 3-way catalyst vehicle. The 3-way catalyst relies on very close control of air-fuel ratio for simultaneous removal of HC, CO, and NO_x. The close control of air-fuel ratio, achieved by a lambda sensor, and low oxygen levels in the exhaust resulted in very low sulfate formation.

The vehicles tested in this program are being operated over the 1975 FTP, the Hiway Economy Cycle, and at 60 mph steady state. The HC, CO, and NO_x emission levels of the four vehicles for which sulfates have been analyzed are given in Table 17. Tables 18, 19, 20, and 21 give the particulate and sulfate emissions of these vehicles over the cold start FTP, hot start FTP, EPA highway economy cycle, and 60 mph steady state.

TABLE 17

Gaseous Emission Results¹ - 1975 FTP gpm

<u>Vehicle and Emission Control System</u>	<u>Number of Tests</u>	<u>HC+σ²</u>	<u>CO+σ</u>	<u>NOx+σ</u>
1975 GM prototype- pelleted catalyst	6	0.73+ 0.23	4.38+ 1.44	2.00+ 0.31
1975 Ford light duty truck prototype- monolith catalyst	5	0.96+ 0.22	8.97+ 1.56	1.76+ 0.21
Datsun with Gould reduction catalyst and monolith oxidation catalyst (25,000 miles)	4	0.88+ 0.09	8.16+ 0.38	0.23+ 0.06
Chevrolet equipped with sonic flow Dresser carburetor	1	1.06	5.01	1.55

1. These tests were run on a Labeco electric dynamometer. Correlation with emissions on a Clayton dynamometer used for certification tests is not known at this time.

2. σ is the standard deviation.

TABLE 17 (CONT)

Gaseous Emission Results ¹ - 1975 FTP gpm

<u>Vehicle and Emission Control System</u>	<u>Number of Tests</u>	<u>HC ± σ</u> ²	<u>CO ± σ</u>	<u>NOx ± σ</u>
Plymouth Fury I Gould Catalyst-0 mi.	3	0.44 ± 0.14	3.92 ± 0.53	0.31 ± 0.01
Volvo Three Way Catalyst	4	0.25 ± 0.03	1.36 ± 0.22	2.41 ± 0.17
Ford Capri Stratified Charge	1	0.22	0.91	0.79
Honda CVCC	3	0.45 ± 0.1	5.43 ± 0.39	1.70 ± 0.02
1977 Ford Prototype	4	0.30 ± 0.06	2.43 ± 0.80	*

* Data being processed

TABLE 18

Particulate and Sulfate Test Results - 1975 FTP (0.033% fuel sulfur)

Vehicle and Emission Control System	Number of Tests	Total Particulates milligrams/mile $\pm \sigma$	Sulfuric Acid milligrams/mile $\pm \sigma$	% Fuel Sulfur converted to Sulfate
1975 GM prototype-pelleted catalyst	8	9 \pm 6	1.1 \pm 1.3	0.4 \pm 0.6 ²
1975 Ford light duty truck prototype-monolith catalyst	5	43.0 \pm 13.7	24.2 \pm 3.2 ¹	11.2 \pm 1.2 ¹
Datsun with Gould reduction catalyst and monolith oxidation catalyst (25,000 miles)	3	40.2 \pm 11.0	11.8 \pm 5.5	7.6 \pm 3.7
Chevrolet equipped with sonic flow Dresser carburetor	1	46.2	7.0	3.2

1-4 tests only

2 - In this and subsequent tables, thru Table 22, the percent conversions were determined by direct averaging rather than a weighted average method.

TABLE 19

1
Particulate and Sulfate Test Results - 1972 FTP-Hot Start (0.033% Fuel Sulfur)

Vehicle and Emission Control System	Number of Tests	Total Particulates milligrams/mile + σ	Sulfuric Acid milligrams/mile + σ	% Fuel Sulfur converted to Sulfate
1975 GM prototype-pelleted catalyst	8	20 \pm 4.9	1.2 \pm 1.5	0.5 \pm 0.8
1975 Ford light duty truck prototype-monolith catalyst	5 4 ²	45.8 \pm 17.3 50.8 \pm 15.5	31.1 \pm 4.9 29.4 \pm 3.6	14.9 \pm 2.7 13.9 \pm 1.6
Datsun with Gould reduction catalyst and monolith oxidation catalyst (25,000 miles)	4	39.2 \pm 19.3	4.3 ³ \pm 1.5	3.2 ³ \pm 0.7
Chevrolet equipped with sonic flow Dresser carburetor	1	19.6	2.4	1.2

1. These data were also used in 1975 FTP calculations
2. One set of data deleted because H₂SO₄ emissions were 50% higher than total particulate emissions
3. Results based on 3 tests because 1 filter was sent to Dow for analysis

TABLE 19 (Cont)

Particulate and Sulfate Test Results - 1972 FTP-Hot Start¹ (0.033% Fuel Sulfur)

Vehicle and Emission Control System	Number of Tests	Total Particulates milligrams/mile + -	Sulfuric Acid milligrams/mile + -	% Fuel Sulfur con- verted to Sulfate
1974 Ford Ranch Wagon	3	32.7 ± 23.6	2.7 ± 4.4	
Fury w/ Gould reduction catalyst and monolith oxidation catalyst (0 miles)	4	13.0 ± 5.2	1.7 ± 0.9	0.6 ± 0.4
Ford w/ 77 system	4	260.9 ± 52.3	139.8 ± 37.5	48.7 ± 15.7
Ford Capri with stratified charge	5	32.7 ± 4.6	(4) 4.3 ± 1.0	(4) 3.8 ± 1.0
Honda CVCC	3	10.9 ± 3.8	0.6 ± 0.1	0.4 ± 0.1
Volvo w/ 3 way catalyst	4	1.7 ± 0.4	0.0	0.0

(4) Only 4 tests

TABLE 20

Particulate and Sulfate Test Results - EPA Highway Economy Cycle (0.033% Fuel Sulfur)

Vehicle and Emission Control System	Number of Tests	Total Particulates milligrams/mile \pm σ	Sulfuric Acid milligrams/mile \pm σ	% Fuel Sulfur converted to Sulfate
1975 GM prototype-pelleted catalyst	16	12.8 \pm 9.8	5.1 ¹ \pm 4.2	3.4 ² \pm 2.6
1975 Ford light duty truck prototype-monolith catalyst	10	86.7 \pm 23.0	46.5 \pm 12.8	31.2 \pm 9.2
Datsun with Gould reduction catalyst and monolith oxidation catalyst (25,000 miles)	6	15.6 \pm 5.4	5.5 ³ \pm 0.9	6.7 \pm 1.3
Chevrolet equipped with sonic flow Dresser carburetor	2	9.6 \pm 3.4	2.2 \pm 0.3	1.5 \pm 0.2
	1. 15 tests			
	2. 14 tests			
	3. 5 tests			

TABLE 20 (Cont)

Particulate and Sulfate Test Results-EPA Highway Economy Cycle (0.033% Fuel Sulfur)

Vehicle and Emission Control System	Number of Tests	Total Particulates + milligrams/mile	Sulfuric Acid milligrams/mile + ✓	% Fuel Sulfur converted to Sulfate
1974 Ford Ranch Wagon	6	$>8.4 \pm 2.5$	$>0.7 \pm 0.8$	
Fury w/Gould reduction catalyst and monolith oxidation catalyst (0 miles)	4	16.2 ± 7.9	5.8 ± 2.4	3.7 ± 1.6
Ford w/ 77 system	8	129.7 ± 25.8	68.6 ± 18.3	33.6 ± 9.0
Ford Capri with stratified charge	6	18.4 ± 2.5	3.4 ± 0.6	4.0 ± 0.8
Honda CVCC	6	4.8 ± 2.6	0.8 ± 0.4	0.7 ± 0.3
Volvo w/ 3 way catalyst	8	1.1 ± 0.5	0.0	0.0

TABLE 21

Particulate and Sulfate Test Results - 60 mph Steady State (0.033% Fuel Sulfur)

Vehicle and Emission Control System	Number of Tests	Total Particulates milligrams/mile \pm \bar{c}	Sulfuric Acid milligrams/mile \pm \bar{c}	% Fuel Sulfur converted to Sulfate
1975 GM prototype-pelleted catalyst	31 ¹	51.7 \pm 31.3	22.8 \pm 14.4	15.0 \pm 9.4
1975 Ford light duty truck prototype-monolith catalyst	17	56.3 \pm 19.7	29.7 ² \pm 11.4	19.4 ² \pm 8.7
Datsun with Gould reduction catalyst and monolith oxidation catalyst (25,000 miles)	13	15.0 \pm 4.2	6.4 ³ \pm 3.3	8.3 ³ \pm 4.5
Chevrolet equipped with sonic flow Dresser carburetor	4	9.0 \pm 2.1	3.5 \pm 0.7	2.3 \pm 0.5

1. The variability apparent from the standard deviation is due to a marked increase in sulfate emissions with time. The 31 tests were run in two periods of testing separated by a period of time. The sulfate values at higher mileage are greater than those at lower mileage. This could be due to higher sulfate storage on the catalyst at low mileage.

2. 16 tests - 1 filter sent to Dow for analysis

3. 11 tests - 2 filters sent to Dow for analysis

TABLE 21 (Cont)

Particulate and Sulfate Test Results - 60 mph Steady State (0.033% Fuel Sulfur)

Vehicle and Emission Control System	Number of Tests	Total Particulates milligrams/mile \pm σ	Sulfuric Acid milligrams/mile \pm σ	% Fuel Sulfur converted to Sulfate
1974 Ford Ranch Wagon	11	$< 7.4 \pm 3.3$	$< 0.4 \pm 0.5$	
Fury w/Gould reduction catalyst and monolith oxidation catalyst (0 miles)	8	43.6 ± 12.4	21.2 ± 6.2	12.9 ± 4.6
Ford '77 system	16	124.5 ± 20.6	71.3 ± 10.7	39.0 ± 9.1
Ford Capri with stratified charge	10	22.6 ± 5.1	6.9 ± 1.9	8.8 ± 2.8
Honda CVCC	9	6.6 ± 3.1	2.3 ± 1.1	2.2 ± 1.0
Volvo w/ 3 way catalyst	16	0.4 ± 0.2	0.0	0.0
Peugeot Diesel *Preliminary Results*	3	171.2 ± 16.0	9.0 ± 2.2	0.98

The values in Tables 18 thru 21 have been compared to the values other investigators obtained for similar vehicles. This comparison suggests the in-house values are somewhat lower than those obtained by other investigators. The comparison of the EPA values versus those obtained by others will continue as more in-house testing is done.

Although the two diesel vehicles were tested and the samples taken, the samples were not analyzed because the analysis system could not currently handle the heavy particulate matter. However, six filters were sent to EPA-ORD, where they were analyzed and the results are included in tables 18 and 21. It should be noted that these values are based on only one test sequence and are strictly preliminary. Nevertheless, they do show that even though the percent sulfur conversion is low the sulfate emissions are high due to the high diesel fuel sulfur content.

The total particulate values for these diesel vehicles are listed in Table 22. One item that must be noted is that the diesel vehicles had high particulate emissions which rapidly clogged the filters preventing complete collection of particulates during the rest of the test. Therefore, the values listed for the transient tests should be considered minimum values.

TABLE 22
Particulate Emission Results

Vehicle	Test Conditions	Number of Tests	Total Particulate (Mg/mi) \pm
Mercedes 220 Diesel (#12-217808)	75 FTP Hot Start LA-4 60 MPH S.S	4 7 10	Over 600 Over 600 327 (\pm 119)
Peugeot 504 Diesel (#504-A90-1800021)	75 FTP Hot Start LA-4 60 MPH S.S. Hiway Economy Cycle	4 4 15 8	Over 200 Over 200 219 (\pm 52) Over 200

Contract Work

OMSAPC has funded a contract with Dow Chemical Company for the past several years to measure particulate emissions from automotive vehicles. Initially, this contract work focused on particulate emissions from cars using leaded fuel. Since 1971-72, emphasis was placed on particulate emissions from cars using unleaded fuel which included a large number of catalyst cars. Particulate measurements in 1972 from a Ford car equipped with Engelhard catalysts showed unusually high particulate emissions. Ford analyzed these samples and found sulfuric acid which was the first indication of this problem.

Since then, Dow has done particulate measurements on a large number of cars as listed below:

TABLE 23

Vehicles Tested at Dow

Honda CVCC
 1973 Opel Diesel
 Peugeot Diesel
 Mazda Rotary (3 cars tested)
 Williams Gas Turbine
 Ford with Engelhard 50,000 mile Catalyst
 (Vehicle 24A51)
 Ford with Engelhard 0 mile Catalyst
 (Vehicle 24A51)
 GM Catalyst Prototype (Pontiac) with Monsanto
 Base Metal Pelleted Catalyst
 Ford Catalyst Vehicle (Vehicle A342-35)
 Capri Stratified Charge
 GM 1975 Catalyst Prototype

The particulate samples collected were either sent to ORD for sulfur analysis or, in a few cases, analyzed by Dow themselves. ORD used X-ray fluorescence to obtain total sulfur content of the filter which was assumed to be all sulfate.

The results of these tests is given in Table 24 and show the Diesel and gas turbine to form definite quantities of sulfate.

OMSAPC is now in the process of obtaining additional characterization data through a contract with Southwest Research Institute. This work is discussed in Section 10.

TABLE 24

Sulfate Emissions for Vehicles Tested at Dow

<u>Vehicle</u>	<u>Driving Cycle</u>	<u>Fuel Sulfur</u>	<u>Sulfate gpm</u>
Ford 24A51 50,000-mile Engelhard catalyst	1975 FTP (glass fiber filter)	0.03%	0.012
	1975 FTP (millipore filter)	0.03%	0.022
Ford 24A51 0-mile catalyst	1975 FTP (glass fiber filter)	0.03%	0.014
	1975 FTP (millipore filter)	0.03%	0.023

Table 24 Cont.

<u>Vehicle</u>	<u>Driving Cycle</u>	<u>Fuel Sulfur</u>	<u>Sulfate gpm</u>
Pontiac-Monsanto base metal pelleted catalyst	1975 FTP (millipore filter)	0.03%	0.010
Chevrolet-Pelleted catalyst (tested previous to Contract 68-01-0480)	1975 FTP	0.03%	0.011
Peugeot Diesel	1975 FTP (millipore filter)	0.35%	0.009
Mazda Rotary	1975 FTP (millipore filter)	0.03%	0.003
Williams Gas Turbine	1975 FTP (millipore filter)	0.03%	0.005
	50 mph (millipore filter)	0.03%	0.004

Section 9 - Sulfate Traps

If it is not possible to control the formation of sulfates in the catalyst, it may be possible to control sulfate emissions after the catalyst by use of a sulfate trap. A sulfate trap is a device, which by chemical reaction or mechanical means, removes sulfuric acid particles and SO₃ from the exhaust gas downstream of the catalyst. Most of the available information on automotive sulfate traps was submitted in response to the March 8th Federal Register notice requesting information on sulfates.

Most of the feasible sulfate traps are chemical traps and involve reaction of the acidic sulfate with a base. Sulfate trap type devices, such as limestone scrubbers, were developed to control sulfur dioxide emissions from stationary sources. These traps have not been previously considered for automotive use. Very few comments were received on sulfate trap other than general comments from GM and Ford and some specific comments from Atomics International.

It is also possible that mechanical traps such as those used for lead particulates could be used for sulfates. These traps are not as technically feasible as the chemical traps.

9.1 Mechanical Traps

The mechanical trap is a centrifugal separator type device used to remove particulates from automotive exhaust. These traps have been developed by DuPont, Ethyl, and PPG and have been demonstrated for lead particulates. It is theoretically possible that sulfuric acid could be removed by this trap if the sulfate particles were condensed into particulates when the exhaust reaches the trap.

Ford commented on mechanical traps stating that exhaust system temperatures were too high to allow condensation of sulfates in the exhaust. EPA measurements of temperatures along standard exhaust systems show this statement to be true. Ford mentions that a heat exchanger could be used to lower the exhaust temperature. However, this heat exchanger would condense the water in the exhaust if a large temperature drop occurred. Ford feels it is virtually impossible to maintain the temperature below the condensation point for sulfuric acid yet above the condensation point for water over a wide range of driving conditions.

EPA can tentatively conclude on the basis of the Ford comments and our own measurements of exhaust system temperatures that the mechanical trap is not a promising sulfate trap.

9.2 Molten Carbonate Traps

Atomics International Division (AI) of Rockwell International stated they had developed and tested an exhaust gas scrubber device which has been effective in removing particulates from automobile exhaust gases. This scrubber works by passing the exhaust gas through a molten alkali metal carbonate eutectic consisting of equal parts by weight of lithium, sodium and potassium carbonates. A paper calculation shows this salt will require changing every 15,000 to 20,000 miles. Removal of particulates in this scrubber is accomplished by both a chemical reaction and wetting of the particulates. Atomics International feels the trap is effective at all temperatures but is most effective when the salt has melted. This trap has been tested to only a very limited extent by passing undiluted exhaust gas through a fiberglass filter and aqueous scrubber. While neither sulfates nor SO₂ were analyzed in general, total particulates were measured and found to be about 90% lower with the trap. One measurement was taken of SO₂ removal which showed a 99% reduction.

However, a major problem with this type of scrubber is potential emission of alkali carbonate itself by entrainment from the trap. Limited data from Atomics International indicate an emission rate at 60-70 mph which corresponds to a 2.2% loss of the scrubbing salt over 15,000 miles. Additional work is needed to determine the magnitude of any problem.

Exxon is examining various sulfate traps under contract to EPA and feels the molten carbonate trap has low potential compared with other possible traps. They cite the above entrainment problem, mention that the trap cannot work until the salt is molten, and feel the molten salt mixture is corrosive and hard to contain. Due to these problems, Exxon does not plan to test molten carbonate traps in their program. Furthermore, the molten carbonate trap is considered less feasible for stationary source SO₂ control than other control systems which makes it a less attractive candidate for automotive application.

9.3 Metal Oxide Sulfate Traps

Metal oxides, such as calcium oxide and aluminum oxide (alumina), are good candidates for use in automotive sulfate traps. Metal carbonates, such as calcium carbonate, can also be used. These substances react chemically with the sulfuric acid forming inert sulfate salts. A trap containing calcium carbonate functions similarly to one with calcium oxide in that the solid compound (calcium carbonate or calcium oxide) reacts with the sulfuric acid. A calcium carbonate trap is different from the molten carbonate trap discussed earlier which uses molten salts at high temperatures. Metal oxide and calcium carbonate scrubbers are used to control stationary source SO₂ emissions. Ford, GM, and Exxon commented on metal oxide sulfate type traps.

Ford has done a paper study on metal oxide sulfate traps and feels calcium oxide would be an effective trapping agent. However, Ford calculates that 250 pounds (a cube of 20 inches on edge) of calcium oxide is required to control sulfate emissions over 50,000 miles. Periodic replacement of the calcium oxide at specified mileage intervals would decrease the size of the trap. Ford also commented that the high CO₂ content of the exhaust converts calcium oxide to calcium carbonate which is also an effective trapping agent. Ford has not done any testing with a calcium oxide sulfate trap.

Ford feels that a sulfate trap containing alumina is more promising and would require 32 pounds of alumina over 50,000 miles. Alumina is the same substance used for catalyst pellets and readily reacts with sulfuric acid. However, the temperature of the trap must be kept low enough to prevent decomposition of aluminum sulfate. Ford also commented that attrition of the alumina could occur from the trap. Any development program on sulfate traps must measure for trap attrition products. Finally, Ford stated that a major design problem with alumina and other compounds is a suitable trap design to assure adequate contact between the alumina and the exhaust gas.

GM has designed and tested a 90 in³ vehicle sulfate trap containing alumina. The sulfate trap was installed on a vehicle with a GM catalyst and tested over the FTP. GM stated that the results of testing over the FTP are inconclusive due to low baseline emissions over the FTP without the trap. Clearly, the trap must be tested under conditions such as 60 mph cruise which results in high sulfate emissions. GM, using slightly different assumptions than Ford, calculates that 10-20 pounds of alumina are needed over 50,000 miles.

Exxon has a laboratory program to test calcium oxide traps. Furthermore, Exxon is under contract to EPA to test and evaluate vehicle sulfate traps containing alumina, calcium oxide, or other promising materials. One potential problem with metal oxide traps is that the sulfate compound formed from reaction with the trapping media with SO_3 is larger in volume than the metal oxide. The trap must be designed to accommodate this expansion.

At this time, it is not possible to make any conclusions about the effectiveness or cost of a chemical sulfate trap. Much more evaluation and testing by various companies is needed.

Section 10 - Plans For Future Work

This section briefly discusses the OMSAPC work that will be done in the sulfate area over the coming year. Plans for ORD work on sulfates are covered in a separate paper. Basically, OMSAPC will assess control technology for sulfates and obtain characterization data. ORD will continue to develop measurement methods, obtain characterization data, help do air quality modeling, and obtain health effects data. In addition to these two broad areas, the EPA Office of Air Quality Planning and Standards will investigate the feasibility of fuel desulfurization and will help in the air quality modeling efforts.

The OMSAPC program is divided into two parts, a contract portion and an in-house portion.

10.1 OMSAPC Contract Work

The two major goals for the OMSAPC contract work are to assess control technology for sulfates and to obtain additional characterization data. The former is being done by Exxon Research and Engineering while the latter is being done by Southwest Research Institute.

The Exxon contract started in June, 1974 and will be completed in March, 1975. This work is divided into the following four overall tasks:

- (1) literature search on aspects of SO_2 oxidation pertinent to automotive sulfate emissions
- (2) assessment of sulfate emissions from non-catalyst vehicles
- (3) determination of factors affecting SO_2 oxidation on catalyst vehicles
- (4) evaluation of sulfate traps.

A plan of performance has been turned in outlining the work to be done in these tasks.

The literature search is almost complete and has obtained information in the following areas:

- thermodynamic equilibrium of SO₂ oxidation
- thermodynamic equilibrium of SO₃ hydration
- kinetics and mechanisms of these reactions with emphasis on materials catalyzing these reactions
- reaction of SO₂ and SO₃ with potential trap materials.

Work on the second task has also started. Sulfate emissions will be measured on a 1974 production car, a rotary engine equipped vehicle, a Honda CVCC, and a Diesel car.

Work on the third task will start when catalyst equipped vehicles are obtained. The effect of the following parameters on sulfate emissions will be obtained:

- catalyst formulation
- air injection rate
- catalyst temperature
- catalyst residence time.

The last task will involve evaluating and testing vehicle sulfate traps. Vehicle testing is already underway on a calcium oxide trap.

As a supplement to the Exxon contract, EPA has also awarded a contract to Monsanto Corporation to act in an advisory capacity to EPA in the Exxon work. Monsanto will independently evaluate the four areas above from the results of the Exxon work.

The second major contract area involves obtaining additional sulfate characterization data. This contract is with Southwest Research Institute and started in June, 1974 and will also be complete in March 1975. This contract involves measuring SO₂ and sulfate emissions from the following cars:

- Monolith Catalyst car
- Pelleted Catalyst car
- Dual Catalyst car
- Pre-1973 car
- 1975 Non-catalyst car
- Diesel Engine Vehicle
- Stratified Charge Engine car.

Sulfate emissions will be measured from the oxidation catalyst cars from low mileage and on through 15,000 miles as mileage is accumulated on the cars. Sulfate emissions will be measured at 30 and 60 mph steady state conditions and over the FTP. Measurements will be made with a dilution tunnel and also, at the steady state conditions, by the absorption method.

In addition to this work, contract work is being planned to assess sulfate emissions from heavy duty Diesels. LDV Diesels, even with their very low fuel consumption, have definite sulfate emissions. It is possible that HD Diesel engines would have substantially greater sulfates.

10.2 In-house Work

Future OMSAPC in-house work will be directed towards testing vehicles to determine sulfate emission factors. The vehicles tested to date are given in Section 8.3. Vehicles scheduled for testing in the future provided OMSAPC can obtain them are:

- GM catalyst prototype (designed to meet statutory HC and CO standard)
- Plymouth catalyst vehicle
- Volvo 3 way catalyst vehicle
- Production model 1975 catalyst vehicles (GM, Ford, Chrysler)
- Texaco Stratified Charge vehicle

Arrangements have been completed to obtain several of these vehicles.

Appendix A2

Gasoline De-Sulfurization

Summary

In 39 CFR 9229-9231 March 8, 1974, EPA asked for submission of data and views on the magnitude of the automotive sulfate emissions, the impact of such emissions on ambient air, and the alternative approaches to controlling such emissions.

The Petroleum Refinery Task Force, ESED, OAQPS, was given responsibility for developing paragraph C, Control of Automotive Sulfate Emissions through Fuel Modification and subsequent review of industry input to this section.

Responses to section C were received from 23 refiner/ refineries operating 85 refineries and representing 55 percent of the United States crude capacity of about 14, 173,000 B/D reporting by the National Petroleum Refiners Association (NPRA) April 12, 1974. several of the larger oil companies, notably Gulf and Standard of California (Chevron) failed to submit responses. The reporting companies, numbers of refineries and crude capacity are given in Attachment I.

While the response level of 55 percent might be considered good for this type of inquiry, the quality of some of the reports, including those from at least two majors, was generally marginal to poor.

General comments were received from NPRA who mailed a questionnaire (see Attachment II) to essentially all the refiners in the United States. As of July 12, 1974, NPRA has received responses from 130 refineries representing about 12.5 million barrels per day or 88 percent of U.S. crude capacity. This data was made available to us at a meeting with NPRA in Washington, D.C. on July 16, 1974.

In summary, individual comments were helpful in providing specific impacts on specific configurations of refineries, and in providing ranges of impacts over a wider spectrum of configurations. A more definitive study has been planned by the PRTF, awaiting only the inputs of these comments. Our analysis of the comments did not find any new or startling data or conclusions, and the PRTF study has been initiated generally; in its original form. The proposed work plan is appended as Attachment III.

Control of Automotive Sulfate
Emissions through Fuel Modifications

I. Introduction

EPA received responses from twenty-three refiners (encompassing eighty-five refineries). This represented fifty-five percent of the United States crude capacity of about 14,173,000 barrels per day (as reported by the National Petroleum Refiners Association April 12, 1974). Several of the larger oil companies, notably Gulf and Standard of California (Chevron) did not submit comments. The reporting refiners, numbers of refineries and crude capacities are given in Attachment I.

While the response level of fifty-five percent might be considered good for this type of inquiry, some of the reports, including those from at least two majors, were of little value.

In addition to the comments received by EPA in response to the March 8 Federal Register notice, at least three additional sources of information have been summarized here in order to complete our current analysis of this alternative approach to controlling automotive sulfate emissions. M.W. Kellogg, under contract to EPA, recently completed an analysis of desulfurization of gasoline. Arthur D. Little, under contract to General Motors, also recently completed an analysis of this subject. Finally, NPRA has completed (although a final report has not been issued to date) an industry survey in which responses were received from refiners encompassing 130 refineries (representing eighty-eight percent of the U.S. crude capacity). A discussion of their preliminary results has been also included.

II. Summary of responses to the Federal Register of March 8, 1974.

A point by point coverage of the comments received in response to the Federal Register is given in this section. The Kellogg and ADL gasoline desulfurization studies and the NPRA survey are summarized in Section III.

C-1 The current sulfur content of crude oils, intermediate refinery fractions, and fuel (by type or grade) and trends and anticipated changes in those sulfur levels taking into account changes required to comply with fuel allocation regulations and the projected demand for low-lead and lead-free gasoline.

The response to this item was quite limited in scope and did not provide us with any significantly new view-points on sulfur trends and their impact on sulfur contents of refinery intermediate streams or products.

The general consensus remains that light Arabian crude containing 1.5 to 2.0 wt percent sulfur should be considered as representative of the swing crude during the 1975-1980 period. No mention was made of the effect of availability of North Slope crude containing 0.8 wt percent crude after 1980. There will be an excess of this crude above West Coast requirement for a number of years and it is probable that some of this might be refined in the Mid-Continent. All agreed that the National average level of sulfur in crude runs would increase as a result of increased sour crude importation. Two refiners, Atlantic Richfield and United Refining, predicted a National average sulfur content of 1.0 to 1.2 wt percent in 1975-80. This level is consistent with that indicated by the American Petroleum Institute in a critique of July 2, 1974, on the M. W. Kellogg reports, "Production of Low Sulfur Gasolines Phase I and II."

Actually, average sulfur values may have limited utility in assessing the impact of producing a lower sulfur gasoline on an individual refinery or even a typical type refinery in a PAD district.

For example, Husky who operates in Wyoming and Utah reported processing a crude mix ranging from 2.0 to 3.0 percent, and produces gasoline averaging about 1500 ppm (above ASTM specifications of 1000 ppm). Koch, located in Minnesota, runs on 90 percent Canadian crudes and reported the average sulfur content of the crude mix to the refinery to be 2.5 wt percent. Extensive desulfurization equipment has been installed by Koch whose unleaded gasoline is expected to have about

550 ppm of sulfur in 1974-75, 300 ppm in 1976-78 and a final reduction to 240 ppm in 1979. An antithesis to this is Derby Refining, Wichita, Kansas, who processes a sweet crude with 0.3 wt percent sulfur and produces a total gasoline pool with 700 ppm of sulfur. Derby expects their unleaded gasoline will contain 300 ppm of sulfur.

Texaco provided, for their refineries, a comparison between 1972 sulfur content of crude, gasoline blending components, and total gasoline pool versus similar projections for 1980. The 1980 case assumes installation of substantial additional hydrotreating facilities, presumably to desulfurize catalytic reformer feed stocks, which essentially keeps sulfur level in products at the 1972 level. Hydrodesulfurization of FCC feedstocks or FCC gasolines was not considered in these assessments. Shell furnished a more detailed breakdown of sulfur contents of light and heavy FCC gasolines but did not project these beyond the current situation. The Shell and Texaco data highlight the range of values reported. The Shell and Texaco data are summarized in the following table.

Sulfur contents of Crudes
Intermediate and Other Products

		<u>Texaco</u>			
		<u>1972</u>		<u>1980</u>	
		<u>Shell</u>		<u>Vol % Blended to Gasoline</u>	
		<u>Sulfur Content wt %</u>	<u>Vol % Blended to Gasoline</u>	<u>Sulfur Content wt %</u>	<u>Vol % Blended to Gasoline</u>
<u>Crude Oil</u>		--	--	1.03	--
		0.42	--	--	--
<u>Gasoline Blending Components</u>					
Butane	5	9	7	30	8
Straight run naphtha	100	14	11	390	11
Light FCC gas	800	18	32	710	29
Heavy FCC gas	1500	13			
Hydrocrackate	2	6	--	--	--
Alkylate	5	10	9	20	10
Reformate	1	30	28	10	38
Other	--	--	13	630	4
Total gasoline	350	100	100	290	100

The FCC gasolines are obviously the major contributors to sulfur content of the pool, 65 to 71 percent based on the Texaco data and essentially 100 percent based on the Shell data. Texaco assigns significantly higher sulfur to butane, alkylate and reformat than does Shell. This is extremely important since the only viable method of providing short range low sulfur lead-free gasoline is by selective blending of low sulfur components.

C-2 and C-3: Quantities of low sulfur gasoline expected to be available by September 1974, and in subsequent years, specifying this information by grade and sulfur content.

The ability of the petroleum refining industry to provide unleaded gasoline of low sulfur content using existing or planned refined capacity through appropriate blending of refinery streams, including consideration of blending products of different refineries or facilities.

In the short range the only viable way of providing low-sulfur, lead-free gasoline is by selective blending of low sulfur components. The refiners made it clear that gasoline blending is a compromise of many and sometimes conflicting requirements. Comments made by Union Oil typify the responses and are summarized below:

1. All gasoline stocks must be blended into products - there can be no left overs.
2. The gasoline produced must meet quality requirements.
3. Volumes produced of each grade must meet marketing requirements.

The most common problem is the FCC gasoline, the main contributor to the sulfur content of the pool. FCC gasoline is low in octane, has a low response to lead because of high sulfur, and directionally would be used in unleaded gasoline.

Lead restrictions in other grades limit octane improvement from lead. To compensate for the FCC gasoline, low sulfur higher octane blending stocks like alkylate and reformat are required. Therefore producing low sulfur gasoline using these low sulfur blending components is an antagonistic requirement and severely limits the ability of the refinery to provide quantities of low lead from existing facilities.

In general the refiners indicated only about 20 to 30 percent of the gasoline pool could be made available as low sulfur unleaded gasoline containing 100 ppm of sulfur. Availability of low sulfur gasoline containing 50 ppm was indicated to be nil. In the following table it will be noted that supplies of 100 ppm low sulfur, lead-free gasoline would meet projected demand only through 1977.

Interchange of blending components, even between refineries operated by the same refiner, was considered impractical based on the contention that segregated facilities were not available for handling by pipeline. Even if piping changes, additional tankage, and other equipment for component segregation were installed, it was the general opinion that such exchange would only marginally increase low sulfur, lead-free supplies.

Unleaded Gasoline Production
Percent of Total Gasoline Pool

	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>	<u>1978</u>	<u>1979</u>	<u>1980</u>	<u>1985</u>
<u>Unleaded (1 sulfur limitations)¹</u>								
EPA ²	7	15	30	44	53	63	72	--
Texaco ⁴	2(300) ³	6(300)	15(300)	26(310)	41(350)	56(350)	68(340)	94(330)
Mobil ⁵	--	14	25	--	42	50	56	100
Kocil ⁶	8(550)	15(550)	20(300)	30(290)	40(290)	50(240)	--	--
Amoco ⁷	--	10	20	30	40	50	60	100
Average of Reported Data	5	11	20	29	41	51	61	98

Low-Sulfur Unleaded (No new facilities)⁸

Mobil	20% at 100 ppm -- ▶							
Exxon	25% at 100 ppm --▶							
Arco	20% to 30% at 100 ppm -- ▶							
Citgo	30% at 100 ppm --▶							
Phillips	20% to 30% at 100 ppm --▶							
Amoco ⁷	25 to 30% at 30 ppm --▶	32%(30) ³	39%(100)	44%(100)	55%(100)			
Koch ⁶	No low sulfur							

1. Percent of gasoline pool projected to be produced as lead-free; it is assumed this is company estimate of lead-free requirements for each year.
2. EPA estimate of lead-free gasoline requirements from Arthur D. Little study on impact of lead additives; regulations, EPA 450/3-74-032a, May 1974. Percentages not averaged with other figures.
3. Numbers in () are ppm of sulfur.
4. Texaco claims some refineries may have sulfur values reaching the ASTM specification of 1000 ppm; leaded gasolines decline from 280 ppm in 1974 to 130 ppm in 1985; this is a volume effect.
5. No sulfur values on individual years were given.
6. Koch processes 90 percent Canadian sour crude; have extensive HDS capacity and are currently installing an FCC feed desulfurization unit to reduce SO₂. Leaded regular decreases from 850 ppm (72% of pool) in 1974 to 190 ppm (45% of pool) in 1979, premium from 580 (20% of pool) to 130 ppm (5% of pool) in 1974 and 1979 respectively.
7. Amoco had 4 scenarios: Base Case all gasolines 1000 ppm; Case A all unleaded 300 ppm, Case B unleaded 100 ppm, Case C unleaded 30 ppm; and in all cases regular and premium at 1000 ppm.
8. All reporting stressed these were average values with some other refineries having no capability to produce low sulfur.

C-4 The current status of desulfurization technology which could be used to reduce gasoline sulfur levels - -:

a and b - Desulfurization Technology

Opinion was unanimous that desulfurization technology is well proven and that the options available for reducing the sulfur content of gasoline are limited. As evidenced in C-1, the gasoline from fluid catalytic cracking (FCC) is the major contributor of sulfur to the gasoline pool. In a high conversion gasoline refinery, the FCC gasoline makes up over 30% of the pool. Sulfur content of the total FCC gasoline may typically run 1000 ppm contributing 300 ppm of sulfur to the pool. Another problem is that the sulfur content of the FCC gasoline is skewed, with the heavy FCC gasoline containing twice as much sulfur as light FCC gasoline. Light straight run naphthas which usually comprise about 10% of the pool may also contain substantial quantities of sulfur, i.e. 100 to 500 ppm. Of course the sulfur contents of these streams are a function of sulfur contents of refinery crude runs as well as the amount of desulfurization equipment operating in the refinery.

Three processing schemes are generally accepted as being applicable to reduction of sulfur in gasoline.

- (1) Desulfurize feed to the fluid catalytic cracking unit, (FCC)
- (2) Desulfurize FCC gasoline.
 - (a) Desulfurize full range FCC gasoline
 - (b) Desulfurize heavy FCC gasoline.
 - (c) Severly desulfurize heavy FCC gasoline; mildly hydrotreat light FCC gasoline.
- (3) Desulfurize light straight run naphtha.

The two companies who supplied the most in-depth analysis spoke to only (1), (2) (a) and (3) above. Simplified flow plans of these options are shown in Figures 1 through 4. The most severe case would be either (1) + (3) or (2a) + (3). Refineries processing high sulfur content crudes would probably be faced with these options. A lower sulfur crude refinery might not opt to use (3) and could possibly make low-sulfur lead-free gasoline using 2(b) only.

It is generally impossible to generalize on which options might be used as they will vary from refinery to refinery. Projection from a single or even several refineries to a National basis can be extremely misleading.

c. Effect on Octane

The minimal effect on octane will be when total FCC naphtha is fractionated into a light (C_5 - 180°F) and heavy fraction (180°F - 430°F) and only the heavy fraction desulfurized. Atlantic Richfield estimates 35 vol percent of C_5 - 180°F, 93 RON clear, could be sent directly to the gasoline pool. Sulfur content of this fraction is about 200 ppm. The 65 vol percent heavy fraction containing 1230 ppm of sulfur would be completely desulfurized and octane reduced from 92.3 to 76 RON clear. The total FCC gasoline would be reduced by 10.2 RON clear. No data were given on MON impact.

Union Oil reported an 8 RON 2 MON reduction if total full range FCC naphtha were hydrotreated. This is not consistent with the Atlantic Richfield data but differences between refineries are to be expected. An average value for desulfurizing full range FCC naphtha is probably in the order of 8 to 15 RON clear.

With FCC naphtha accounting for about 30 percent of the gasoline pool full range naphtha treating would cost about 3.0 to 4.5 RON (less than 1 MON) clear octane numbers.

d.thru i. - Impact on the Industry - Time, Cost, Energy

Construction Impact

Leadtimes for individual refiners to have the capability to supply all of their gasoline with a limit of 100 ppm sulfur ranged from zero to greater than six years depending upon the current desulfurization capabilities and crude supplies of each refiner. The median response was four years, but most refiners added that leadtimes may be much longer because of the large amount of construction planned to increase total refining capacity.

Capital Investment

Capital investment estimates for individual refiners ranged from zero to \$994 million for the manufacture of 100 ppm sulfur gasoline for a refiner with eleven

refineries to \$1,445 million for the same refiner to manufacture 50 ppm sulfur gasoline. However, the second highest estimate was \$257 million and most refiners' estimates were between 30 and 200 million dollars. The data were insufficient to determine the cost for a typical or average refiner or refinery. Only three comments included an estimate for the total industry impact. The Mobil and Atlantic Richfield estimates were \$2.5 billion and \$2.0 billion respectively. However, the Texaco estimate was much greater -- \$12 billion. Preliminary results of the survey by the National Petroleum Refiners Association indicate a capital cost of approximately \$3.7 billion.

Operating Costs

Refiner incremental operating costs were estimated by only three companies. For 100 ppm sulfur, Cities Service and Exxon estimated \$12 million per year and Texaco estimated \$200 million per year. For 50 ppm sulfur, Cities Service and Exxon estimated approximately \$30 million per year and Texaco estimated \$230 million per year. Costs per gallon of gasoline ranged from 0.5 to 2 cents per gallon with only five estimates.

Energy and Yield Impacts

Energy penalties were estimated by only six companies and range from 1/2% to 1 1/2% on crude. These estimates are difficult to assess because of the variety of processing schemes and methods of calculation of penalties.

Yield penalties were estimated by three companies for constant crude input. The yield losses shown were approximately 1 to 2%. Again, the estimates are difficult to assess because of the differences in calculation procedures.

Industry Impact¹

	<u>Range</u>	<u>Median</u>
Construction leadtime	0 to 6 years	4 years
Capital investment	\$2 to 12 billion	\$2 1/2 billion
Annual operating costs	\$12 to 200 million	\$12 million
Cost per gallon of gasoline	0.5 to 2.0 cpg	1 cpg
Energy penalty	1/2 to 1 1/2%	1%
Gasoline yield penalty ²	1 to 2%	1%

Note:

¹ 100 ppm sulfur

² At constant crude input

C-5 Impact of industry-wide adoption of desulfurization technology.

a and b Impact of gasoline desulfurization on refinery flexibility.

Gasoline desulfurization using the technology described in C-4 is not expected to have an appreciable affect on the refinery flexibility to vary product yield patterns. This is not so in the early years 1975-79 prior to installation of desulfurization facilities. The greatest portion of the sulfur is contained in the heavier portion of FCC gasoline. This fraction is a seasonal swing item, going into gasoline in the summer and heating oil in the winter. Thus sulfur restrictions could limit ability to maximize gasoline in the short term.

c. Feasibility of desulfurizing only lead-free vs total pool.

Only certain gasoline blending components need to be desulfurized to meet various sulfur restrictions. If lead-free gasoline gradually increases to essentially 100 percent it is probably most economical to size the desulfurizers to treat these components to meet those ultimate requirements. For example, desulfurization of all FCC gasoline would be more practical than just the portion needed for lead-free. Furthermore, the time frame required for construction of facilities to desulfurize only lead-free is the same as for total gasoline.

d. Impact of various degrees of gasoline desulfurization on sulfur content of other fuels.

If FCC gasoline desulfurization is selected as the process to meet gasoline sulfur specifications, the affect on the sulfur content of other products is negligible.

Desulfurization of total FCC feed stock would reduce the sulfur content of No. 2 Distillate.

C-6 Contribution of fuel additives to gasoline sulfur content.

The two refineries who reported on this item stated their additives contributed about 5 to 7 ppm sulfur to the gasoline pool.

III. Other Studies

A. Kellogg - Low Sulfur Unleaded Gasoline

In order to obtain a quick analysis of the impact of desulfurizing gasoline, EPA contracted M. W. Kellogg Company for a three-phase study to be completed by early summer 1974. The draft final report of Phase 3 was completed in July. Phases 1 and 2 assess the impact, on a typical U.S. refinery, of producing low-sulfur (60 ppm), unleaded gasoline. (Phase 2 is essentially a better-calibrated version of Phase 1.) The major conclusions of the Kellogg Phase 2 report are that a typical existing refinery can produce sufficient quantities of low-sulfur, unleaded gasoline by blending current low-sulfur streams until 1976, while maintaining refinery product outputs. In order to manufacture more low-sulfur, unleaded gasoline than blending allows in later years, the refinery is allowed a choice of two desulfurization schemes: (1) hydrodesulfurization of cat cracker feed and light virgin and light coker (or thermal) gasolines and (2) hydrodesulfurization of cat cracked gasoline. Phase 2 calculates that the cat cracked feed desulfurization route would require an incremental cumulative capital investment of \$2.0 billion for the United States and an incremental operating cost of 0.7 to 1.6 cents per gallon of total gasoline (for refinery sizes of 100,000 to 16,000 barrels per calendar day) to produce low-sulfur unleaded gasoline thru 1979. After 1979 additional (unspecified amount) octane improvement facilities would be necessary. Phase 3 of the Kellogg study evaluates the same scenarios for a typical California refinery. Phase 3 concludes that a typical existing California refinery can manufacture low-sulfur, unleaded gasoline until 1976 by blending current low-sulfur components. After that, hydrodesulfurization of cat cracker feed and light virgin gasoline and light thermally cracked gasoline, would cost \$280 million (for the 1.4 billion barrel per stream day (bpsd) capacity of the eleven California refineries larger than 75,000 bpsd, i.e., 78 percent of the total California capacity) and 1.1 cents per gallon of total gasoline. The alternate route of

desulfurization of cat cracked gasoline would cost \$200 million incremental investment and 1.0 cents per gallon incremental manufacturing cost. Furthermore, additional facilities (unspecified amount) would be required to replace the octane lost by hydrodesulfurizing the gasoline.

As with any study of the petroleum industry, the input assumptions and calibration and flexibility of the model are extremely important. The EPA-required lead phase-down is not included in the base scenario. Rather, the base is an existing "typical" refinery producing current grades of gasoline. The study then assesses the incremental impact of manufacture of low-sulfur, unleaded gasoline on that refinery. A more realistic base (or a first-step) scenario would include the unleaded introduction rate and the lead phase-down schedule in order to account for refinery commitments to meet those requirements (which have been known for the last few years) before assessing the incremental impact of a sulfur specification. In regard to calibration and flexibility of the model, it should be noted that several simplifying assumptions were used in the Kellogg study because of the constraints of providing a timely analysis. For example, reformer severity, cat cracker conversion, and alkylate production volume were fixed and aromatic production was assumed to be part of total reformate rather than utilizing a separate reformer. The degree of impact of these simplifying assumptions can not be quantified without additional modeling.

B. Arthur D. Little - Low Sulfur Unleaded Gasoline

As a result of concern over sulfate emissions and in response to the EPA request for information on this potential problem, General Motors Corporation (GM) commissioned Arthur D. Little, Incorporated (ADL) in April of 1974 to study the ability of the U.S. refining industry to produce low-sulfur, unleaded gasoline. The final report was completed in June. The ADL study assesses the impact, on a composite U. S. gasoline refinery, of reducing the sulfur content of unleaded gasoline to approximately 100 ppm and 30 ppm for the period 1975-1985. The

penetration rate of unleaded gasoline and the lead phase-down schedule were incorporated in the base scenario. For simulations of the years 1975 and 1976, the model configuration was restricted to the present ratio of downstream processing capacity to crude distillation capacity. However, the simulations for post-1976 were allowed complete flexibility to determine future refinery processing requirements, including direct desulfurization of gasoline, desulfurization of cat cracker feed, and increased use of hydrocracking. The major conclusion of the ADL study is that for the 1975 to 1979 time period there is essentially no increase in refinery desulfurization processing capacity required to manufacture low-sulfur (both the 30 ppm and 100 ppm cases), unleaded gasoline. That is, until 1980, the low-sulfur, unleaded gasoline can be manufactured by selectively blending sweet components into the unleaded grade. Beginning in 1980, when the unleaded gasoline volume first exceeds 50 percent as forecast by GM, significant hydrodesulfurization/hydrocracking capacity must be added. By 1985, the incremental impact of reducing the sulfur content of unleaded gasoline to 100 ppm would require a \$2.3 billion cumulative incremental investment (1974 dollars) and an incremental manufacturing cost (including delta raw materials, by-products, capital charge, and operating cost) of 0.62 cents per gallon of unleaded gasoline. The impact for 30 ppm would be \$7.5 billion and 1.35 cents per gallon.

As mentioned above, the input assumptions and calibration and flexibility of the model are extremely important for any study of the petroleum industry. As ADL notes in the study, an overview considering the entire U.S. refining industry as a single composite model has inherent limitations. The extent of these limitations can only be quantified by additional studies. ADL states that their composite model reasonably represents the flexibility and economics of the large volume gasoline manufacturers which supply the majority of the market place, although their analysis does not address itself to regional variations or the specific problems of small or atypical refiners. Further, the ADL study did not attempt to assess the ability of the construction industry to respond to the incremental

investment required. This is clearly an important variable which must be properly evaluated, especially for the 1974-1980 time period.

C. National Petroleum Refiners Association

In May 1974, the National Petroleum Refiners Association (NPRA) began a survey of the industry to assess the impact of manufacturing low-sulfur, unleaded gasoline. As of July 12, 1974, NPRA had received responses from 130 refineries representing about 12.5 million barrels per day or 88 percent of U.S. crude capacity. These data were made available to EPA at a meeting with NPRA in Washington, D. C. on July 16, 1974. The survey indicates that approximately 25 percent of the gasoline output can currently be made as low-sulfur (100 ppm), unleaded. Also, ten refineries, with a total crude capacity of 607,000 bpsd (approximately 4.3 percent of the U.S. capacity) can make 100 percent of their gasoline as low-sulfur, unleaded now. For the other refineries to manufacture 100 percent as low-sulfur, unleaded would require a median of 4 years construction lead time and approximately \$3.7 billion incremental investment. Included in this investment would be 510 million standard cubic feet per day of hydrogen production, 2100 tons per day of sulfur recovery, 1.9 million bpsd of cat cracker feed desulfurization, 0.8 million bpsd of naphtha desulfurization, 0.6 million bpsd of reforming, and 49,000 bpsd of isomerization.

Attachment I

Refineries Responding to 39 CFR 9230, March 8, 1974

Section C - Control of Automotive Sulfate Emissions by Fuel Modifications

Refiner/Refineries	>100,000 Barrels per day- Total Crude Capacity B/D	Number of Refineries	<100,000 Barrels per day ¹ Total Crude Capacity B/D	Number of Refineries
Amoco Oil Co.	1,027,000	10	Becon Oil Co.	12,100
Atlantic Richfield Co.	776,500	5	Crystal Oil Co.	14,700
Cities Service Co.	268,000	1	Derby Refining Co. ³	26,000
Exxon Corp. (USA)	1,203,000	5	Fletcher	15,000
Koch Industries, Inc.	122,000	1	Husky	45,800
Mobil Oil Corp.	918,000	9	Mohawk	22,000
Phillips Petroleum Co.	397,000	6	Plateau	5,000
Shell Oil Co.	1,087,000	8	Skelly ²	71,000
Texaco, Inc.	1,091,000	11	Southland Oil Co.	21,000
Union	446,000	4	Tenneco, Inc.	88,000
			Tesoro Petroleum Corp.	63,000
			United Refining Co.	48,700
			Witco Chemical	27,000
	7,335,000	60		459,300
Crude capacity reported	7,794,300		Number of refineries reported	85
Total U. S. crude capacity	14,173,000 ¹		Total number	263 ⁴
Percent reported	55		Percent reported	32
			Percent >30,000B/D reported	40

1. NPRA (FEA) data 4-12-74.

2. Owned by Getty.

3. Owned by Coastal States Gas Producing Company.

4. Includes 49 refineries <10,000 B/D with capacity of 169,000B/D
50 refineries 10 to 30,000 B/D with capacity of 719,000 B/D.

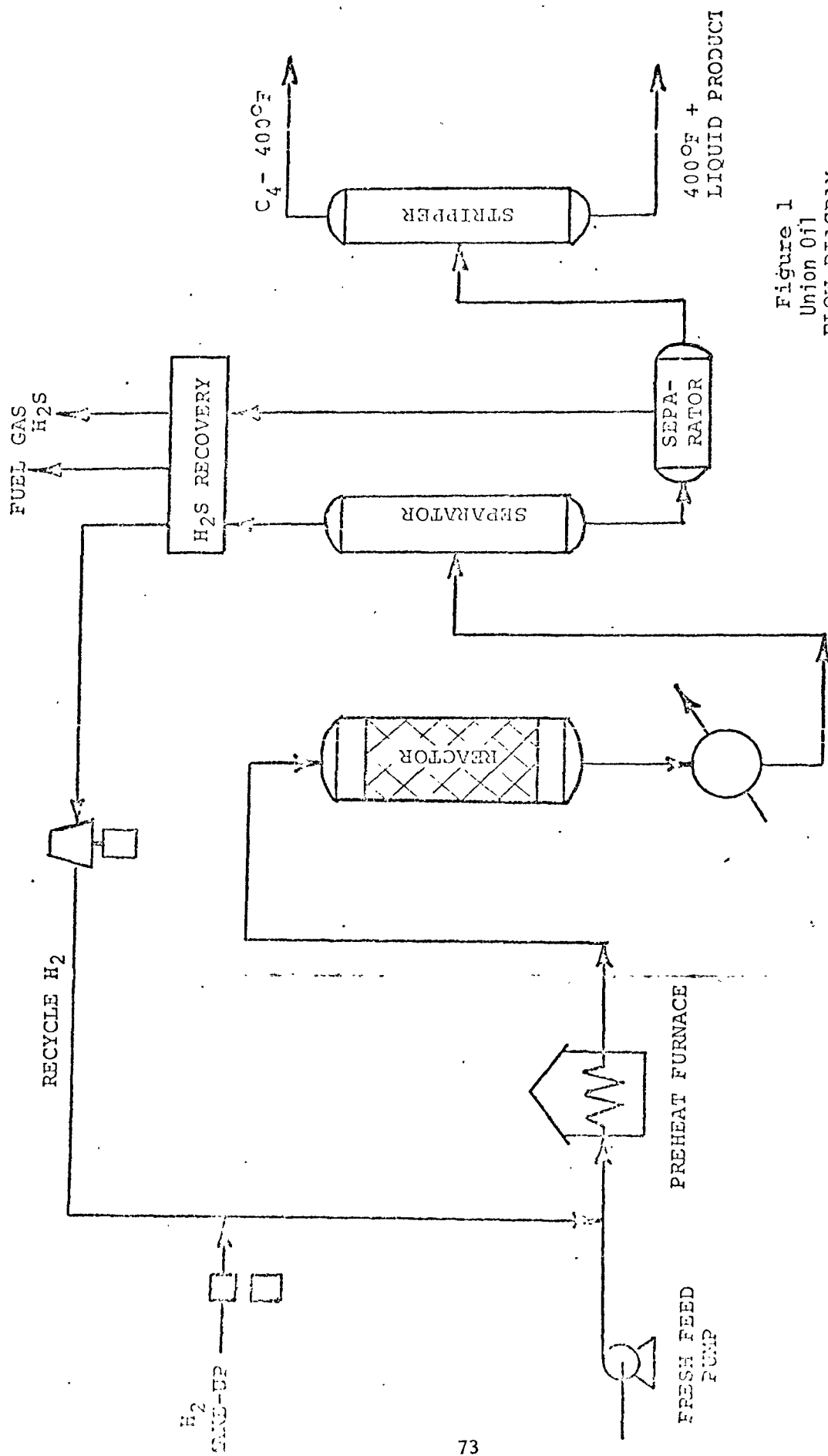


Figure 1
Union Oil
FLOW DIAGRAM OF
DESULFURIZATION OF
FCC FEEDSTOCKS

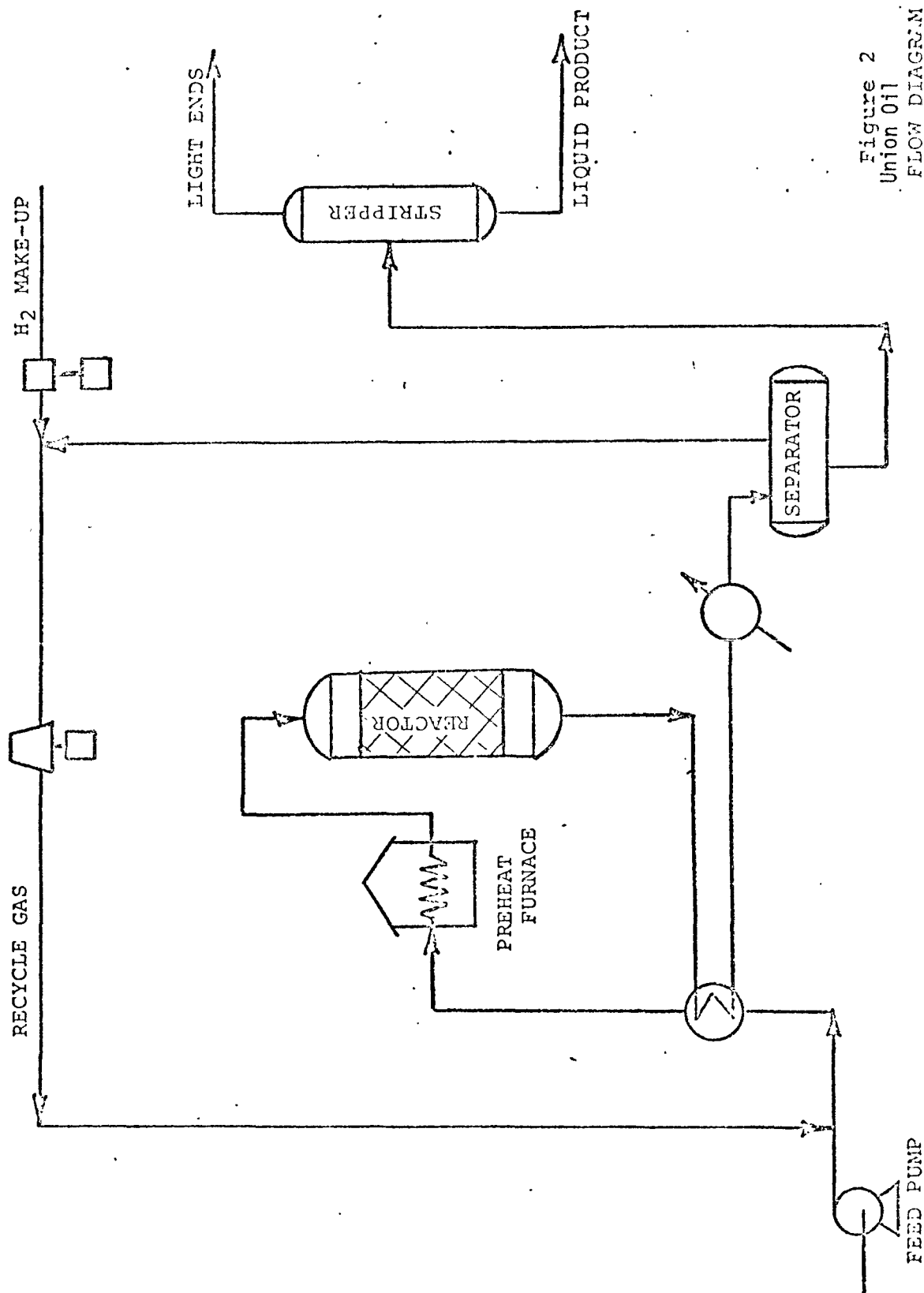


Figure 2
 Union Oil
 FLOW DIAGRAM
 NAPHTHA UNIONIZING
 FOR FULL RANGE FCC GASOLIN

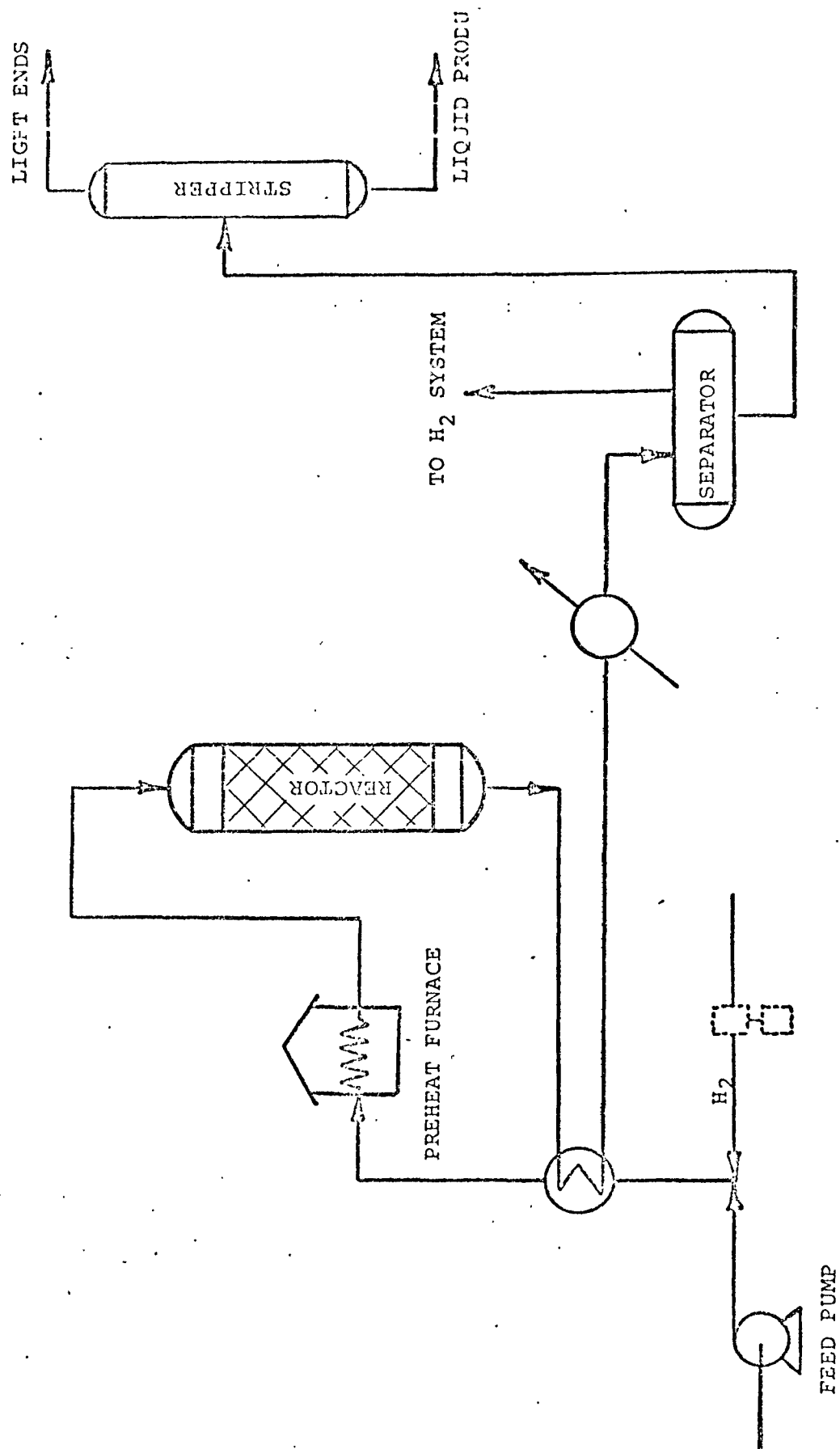
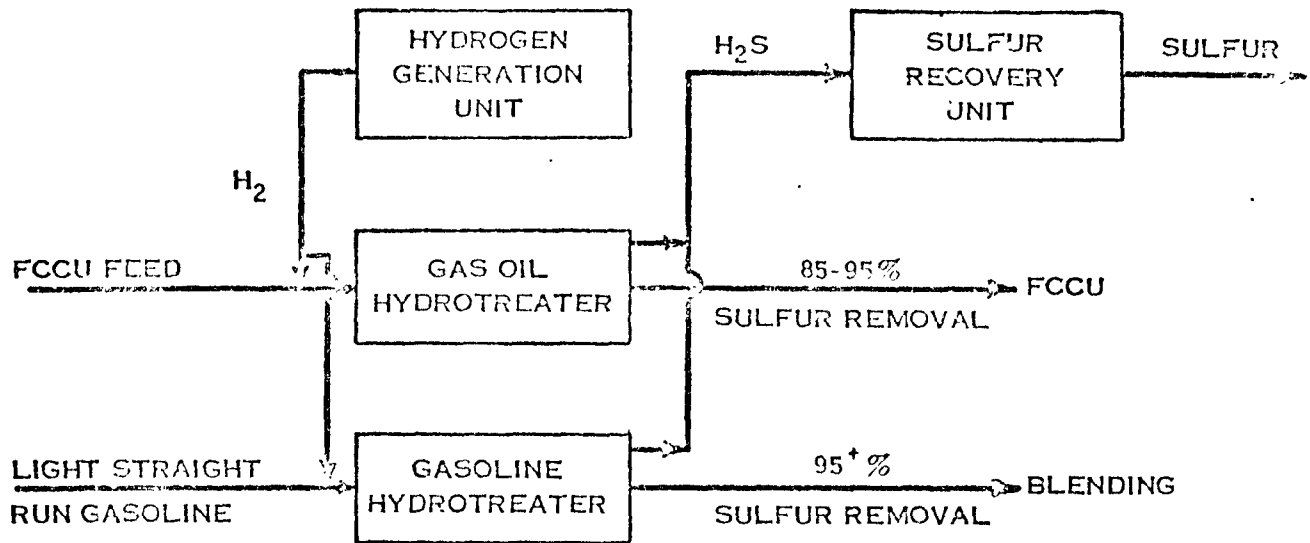


Figure 3
Union Oil
FION DIAGRAM
UNIONFINING OF LSR NAPHTHA

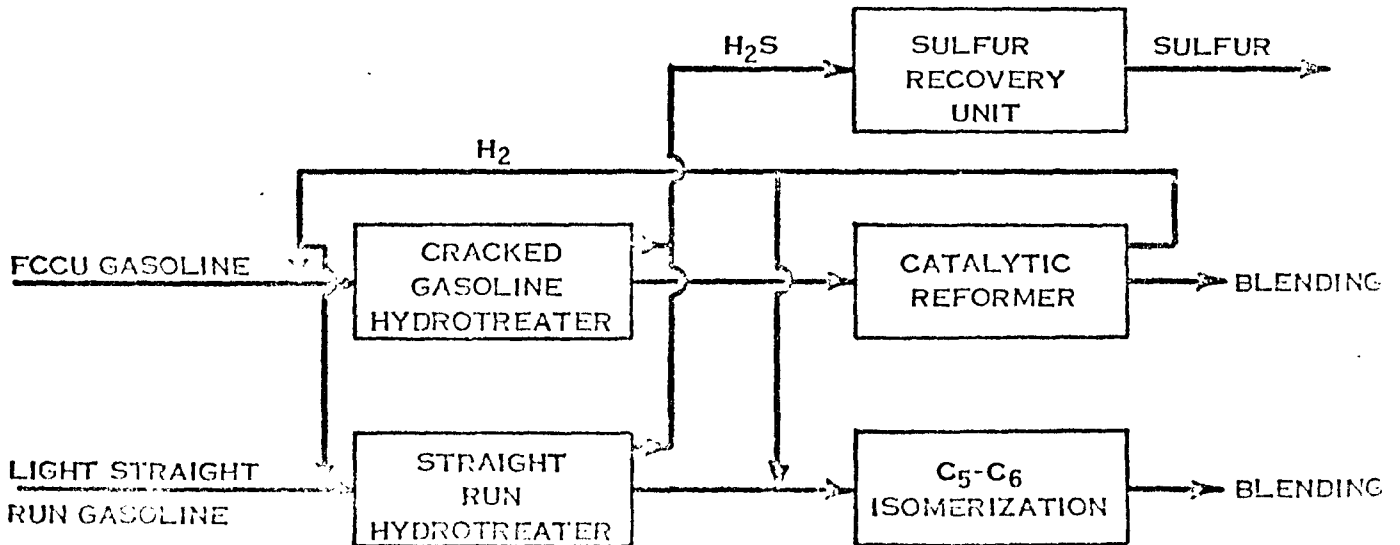
FIGURE 4

ADDITIONAL FACILITIES REQUIRED TO LOWER
SULFUR CONTENT OF THE GASOLINE POOL

Texaco
SELECTED OPTION



Texaco
ALTERNATE OPTION



NPRA SURVEY OF
U.S. DOMESTIC PETROLEUM REFINING INDUSTRY'S
CAPABILITY TO MANUFACTURE LOW-SULFUR
UNLEADED MOTOR GASOLINE

A. Introduction

In the March 8, 1974 Federal Register, the Environmental Protection Agency expressed concern over the sulfate emissions from automobiles equipped with catalytic converters and requested information on alternative control systems including "Control of Automobile Sulfate Emissions Through Fuel Modifications."

The National Petroleum Refiners Association has completed a survey of the U.S. domestic petroleum refining industry to develop information concerning the impact of reducing the sulfur content in unleaded gasoline to 100 parts per million (100 ppm) during the period 1974 - 1980.

A survey questionnaire was sent to each petroleum refining company to be completed for each refinery which had the capability to manufacture finished motor gasoline. The survey was designed to give not only an overall picture of the effects of unleaded gasoline sulfur control but also to demonstrate the large variation between refineries in the industry's current capability to manufacture low-sulfur unleaded gasoline and the need for additional process facility requirements.

Survey responses were received from refiners operating 148 refineries, having a combined crude charge capacity of 13.2 million barrels per day (b/d). The data in this report represents more than 90% of the U.S. crude processing capacity and approximately 95% of the finished gasoline manufacturing capacity.

The individual refinery data in the accompanying Tables have been tabulated by three capacity categories:

- | | | |
|-------------------------|----|------------------|
| 1) 100,000 b/d and over | -- | (46 refineries), |
| 2) 30,000 - 99,999 b/d | -- | (63 refineries), |
| 3) under 30,000 b/d | -- | (39 refineries). |

Within the first category, the capacities of the 16 largest refineries have been combined and the refineries listed randomly in order to maintain the confidentiality of data due to the uniqueness of their capabilities.

B. Survey Results

Table 1 summarizes the \$3.7 billion industry capital investment and 361 facilities which are projected to be needed in the period 1974 - 1980 for the manufacture of low-sulfur (100 ppm) unleaded gasoline by the 148 refineries in the survey.

The majority of survey respondents stated that it would not be economically feasible to provide for the incremental (i.e. 50%) construction or expansion of desulfurization facilities, if the entire gasoline pool would eventually be desulfurized. Therefore, the total projected capital investment of \$3.7 billion would be expended at the time desulfurization of unleaded gasoline was mandated. It is important to note that this expenditure has been estimated in 1974 dollars and that by the time the money would actually be spent in the late 1970's the amount would be much higher.

The adverse impact on the small and medium size refineries is apparent from reviewing the range and average costs per barrel of refinery capacity shown in Table 1. Desulfurization of the total unleaded gasoline pool of these refineries would result in a per barrel cost of more than double that of the large refineries. The variation in the per barrel costs are due in part to different crude types, sulfur content of crudes, refinery size and process configurations.

Respondents to the survey indicated six categories of additional process plants would be needed to provide the capability to desulfurize unleaded gasoline during the period 1974 - 1980. The capacities and number of these new process facilities are summarized in Table 2 for each refinery size category. Here again, the adverse impact on small and medium size refineries of desulfurizing unleaded gasoline is substantiated by the fact that they will need a total 242 new process facilities for their 4.3 million b/d of crude capacity while the large refineries will only require 119 new process plants for their 8.9 million b/d of crude capacity. The number of new plants is perhaps more important than capacity in that technical manpower is more closely related to the number of plants. Survey respondents believe that it is not within the capability of the already overloaded engineering/construction industry to complete these desulfurization facilities in the short term (3 years) while simultaneously constructing refinery facilities to meet the country's increased energy demands.

The present extended refinery construction periods, due largely to the recent doubling or tripling of the time required for delivery of many major equipment items, are widely recognized as a major problem in the U.S. energy picture. This situation is not expected to ease and may become tighter even without the imposition of more stringent sulfur specifications for unleaded gasoline.

Tables 3, 4, and 5 delineate the additional capacity of process facilities needed to manufacture low-sulfur (100 ppm) unleaded gasoline. Those refineries having no capital investment costs shown either did not require additional desulfurization facilities or did not report on plans to install additional gasoline facilities. The large variation in additional process capacities and investment costs for new desulfurization requirements is amply demonstrated upon a review of these three Tables.

Table 6 summarizes the current capability of respondents to manufacture low-sulfur (100 ppm) unleaded gasoline. Although the average capability to make this fuel is about 30% of the gasoline pool of refinery respondents, it is distributed such that 49 refineries with a crude capacity of 3.6 million b/d, can only manufacture less than 10% of their gasoline stocks as low-sulfur unleaded gasoline.

As can be seen from the Table, 38 refineries operated by 16 companies, can currently manufacture over 30% of their gasoline pool as low-sulfur unleaded gasoline. This capability amounts to about 1.2 million b/d. Although this volume of low-sulfur unleaded gasoline appears adequate to satisfy the expected 1975 demand, any regulation by the EPA and FEA requiring the nationwide distribution of low-sulfur unleaded gasoline would be severely disruptive due to the limited production base. Moreover, logistic problems involving segregated storage, component exchanges, quality control, and transportation of this sterile fuel would certainly result in additional costs. With such a limited manufacturing base, any regulation further limiting the sulfur content of unleaded gasoline could not be very effective until significant capital expenditures and refinery construction efforts are consummated.

Tables 7, 8 and 9 show the anticipated average weight per cent of sulfur in the respondent's crude oil and gasoline pool for 1974 and 1980. For all categories of refineries, trends in crude supplies are in the direction of increasing sulfur content with the larger refineries indicating significant increases in sulfur while the small refineries show only nominal increases. Further analysis of the sulfur content of gasoline pool of the refinery respondents reveals a slight increase in the sulfur level in the large and medium size refineries while the small refineries expect to have essentially the same sulfur level in the gasoline pool.

The projected capital investment, for desulfurization facilities detailed in Tables 3, 4 and 5 correlate quite closely to the sulfur data shown in these Tables.

Finally, although the data on energy consumption directly associated with the desulfurization of unleaded gasoline varied quite widely, it is estimated that an increase in energy requirements of between 100,000 - 200,000 b/d of equivalent fuel oil (approximately 1% of crude charge) would take place; and, depending on the processing method selected, additional losses in gasoline and other products yields could result.

Although no quantitative data were requested, refiners were asked to discuss the possibility of producing unleaded gasoline with 50 ppm of sulfur. Many responded that they did not know how this could be done consistently. It should be noted that to guarantee a 50 ppm maximum sulfur level in the finished unleaded gasoline, the sulfur levels would have to be much lower to allow for plant upsets and gasoline blending flexibility.

C. Conclusions

The ramifications of desulfurizing unleaded gasoline to the level of 100 ppm or less, as detailed in the preceding sections, provide sufficient justification in pursuing a cautious and comprehensive approach before either proposing or promulgating regulations to desulfurize unleaded gasoline as a means of controlling automotive sulfate emissions through fuel modifications. The critical energy and inflation problems of our nation demand that we seek and achieve the solution which enhances our energy self-sufficiency while effectively curbing inflation.

TABLE 1

CAPITAL INVESTMENT REQUIREMENTS TO
MANUFACTURE LOW-SULFUR (100 ppm) UNLEADED MOTOR GASOLINE

Refinery Category	No. of Refineries	Capacity (million b/d)	No. of New Facilities	Investment Costs (billion \$)	Range (\$/bbl)	Avg. Cost (\$/bbl)
>100,000 b/d	46	8.9	119	1.9	0-867	212
30,000-99,999 b/d	63	3.7	156	1.5	0-1,518	404
<30,000 b/d	39	.6	86	.3	0-2,588	500
TOTAL:	148	13.2	361	3.7		

NOTE: The cost per barrel figures shown were calculated using the proposed capital investment and the crude capacity for each refinery in order to evaluate the impact on refineries of desulfurizing unleaded gasoline.

TABLE 2
NEW PROCESS CAPACITY NEEDED TO
MANUFACTURE LOW-SULFUR (100 ppm) UNLEADED MOTOR GASOLINE

Process Category	Refinery Category			Total
	100,000 b/d and over	30,000-99,999 b/d	under 30,000 b/d	
FCC Feed Treating (M b/d)	1,283 (30)	729 (38)	130 (19)	2,140 (8)
Naphtha/Gasoline Treating (M b/d)	394 (27)	406 (42)	90 (21)	889 (9)
Catalytic Reforming (M b/d)	317 (19)	264 (23)	44 (12)	625 (5)
Isomerization (M b/d)	25 (4)	25 (8)	---	50 (1)
Hydrogen Plant (MM scf/d)	320 (20)	161 (19)	35 (13)	514 (5)
Sulfur Plant (Tons/d)	1,100 (19)	732 (26)	223 (21)	2,055 (4)
Total	(119)	(156)	(86)	(3)

NOTE: Figures in parenthesis are the number of new facilities reported to be needed for the related process capacity by 1980.

NEW PROCESS CAPACITY REQUIREMENTS TO
MANUFACTURE LOW-SULFUR (100 ppm) UNLEADED MOTOR GASOLINE

Refineries with 100,000 and over b/d capacity

Refinery Capacity (M b/d)	FCC Feed Treating (M b/d)	Naphtha/Gasoline Treating (M b/d)	Catalytic Reforming (M b/d)	Isomerization (M b/d)	Hydrogen Plant (MM scf/d)	Sulfur Plant (Tons/d)	Capital Costs (\$ million)
1.							50.0
2.	105	15					120.0
3.							20.0
4.	87		87		8.8	28.9	112.0
5.	50				15	50	120.0
6.	150				65	200	197.4
7.	35						22.0
8.		5	5				9.0
9.	50	18					72.0
10.							55.0
11.		7.5	7.5				12.7
12.	30	15					71.0
13.		33	42		8	9.5	30.0
14.	69				19		39.0
15.		12	12				21.0
16.		17	17				29.7
17.	190						0.0
18.	190						0.0
19.	130	40	40				45.2
20.	180	70			10	35	68.0
21.	170						0.0
22.	170						0.0
23.	170	57			20		35.0
24.	170	25				1.6	15.4
25.	170	20				19	27.9
26.	150	60	15		20	100	80.0
27.	150	75			40	200	116.6
28.	140	60			30	200	63.0
29.	140						0.0
30.	140	56			30		51.0
31.	130	55				26	34.4
32.	130	48			16		29.0
33.	120	52			16	50	50.0
34.	120	6	22	10			16.0
35.	120	40			10	40	20.0
36.	120						0.0
37.	110	20	7				6.0
38.	110		25				13.0
39.	110	35	32				53.0
40.	110		20				27.7
41.	110	10	10	12			11.1
42.	100	15.5	89			115	91.1
43.	100						0.0
44.	100		30				28.4
45.	100		3.1	3.1	2.3		8.5
46.	100	27			10	25	5.3
Totals	8,900	1,282.5	393.6	316.5	25.1	320.1	1,923.4

* Total capacity of 2.59 million b/d for refineries larger than 300,000 b/d.

** Total capacity of 2.21 million b/d for refineries larger than 200,000 b/d.
(Refineries grouped together to maintain confidentiality of data.)

NEW PROCESS CAPACITY REQUIREMENTS TO
MANUFACTURE LOW-SULFUR (100 ppm) UNLEADED MOTOR GASOLINE

Refineries with 30,000-99,999 b/d capacity

Refinery Capacity (M b/d)	FCC Feed Treating (M b/d)	Naphtha/Gasoline Treating (M b/d)	Catalytic Reforming (M b/d)	Isomerization (M b/d)	Hydrogen Plant (MM scf/d)	Sulfur Plant (Tons/d)	Capital Costs (\$ million)
1. 95							
2. 95		5		5	4.8		0.0
3. 90							12.8
4. 90	30						0.0
5. 90		10				17	21.4
6. 90	50						13.0
7. 85		30	20		25	50	108.9
8. 85	33						17.4
9. 85		28	8				18.0
10. 85		20	20				21.0
11. 85		20	20				24.7
12. 85	35						23.3
13. 85					25	50	96.2
14. 75	75	16.5					25.0
15. 75	15						13.0
16. 70		24	8		15	40	44.0
17. 70		23					18.0
18. 70	20	8					13.0
19. 70			14				22.0
20. 70	35						10.0
21. 70					25	50	96.2
22. 65	16	11	10				7.0
23. 65			2.6				4.8
24. 65	10				5		5.5
25. 65			2.5		5		14.2
26. 65	35				10		6.0
27. 60		25	25		25	50	96.2
28. 60		22	22				46.0
29. 60	47		50				39.8
30. 55	12.5					150	44.9
31. 55	25						6.0
32. 55	41	7.5				9	16.6
33. 55		10				33.5	25.3
34. 50		14					37.0
35. 50	11.1		6.1	5	5	33	25.5
36. 50	24	2			1.25	2	21.0
37. 50	12	15	15			22	21.9
38. 50		10					32.0
39. 50	27	26					5.0
40. 50	13					30	33.3
41. 50	25						10.0
42. 45		7	14	7	10	40	75.9
43. 45	15	4				55	29.3
44. 45		6			2	20	11.0
45. 45	8	10					3.0
46. 45	18						38.0
47. 45							25.0
48. 40							15.0
49. 40		5.3					0.0
50. 40	15	5					3.6
51. 40		4	4			15	9.7
52. 40	15						7.5
53. 40		8			3	15	16.9
54. 40	8						4.0
55. 40						5	22.3
56. 40							4.0
57. 35	12	10		4			0.0
58. 35	14	7.1	9	0.8		15	15.6
59. 35		3				30	53.1
60. 35	6.1	1.8	5.8	3			.5
61. 30							6.8
62. 30	12.5						0.0
63. 30	14	8	8				6.0
Totals	1,462.6	729.2	406.2	264.0	24.8	161.05	731.5
							1,462.6

NEW PROCESS CAPACITY REQUIREMENTS TO
MANUFACTURE LOW-SULFUR (100 ppm) UNLEADED MOTOR GASOLINE

Refineries with less than 30,000 b/d capacity

	Refinery Capacity (M b/d)	FCC Feed Treating (M b/d)	Naphtha/Gasoline Treating (M b/d)	Catalytic Reforming (M b/d)	Isomerization (M b/d)	Hydrogen Plant (MM scf/d)	Sulfur Plant (Tons/d)	Capital Costs (\$ million)
1.	29	16						9.0
2.	29							0.0
3.	29		14			2		13.2
4.	29	17				3.6	25	17.1
5.	27		6	6				7.2
6.	27		3.6				5	3.0
7.	26	8		5				5.5
8.	26		7	4				5.5
9.	25	10				4.5	25	10.4
10.	25	10	7			2.8	25	6.6
11.	25		5					8.0
12.	23	10	2.5					6.0
13.	23		5	5				10.9
14.	22		14.3	14.3			6	12.0
15.	22		8	4				5.6
16.	21	9				1.8	9	11.3
17.	21	10				5	25	44.0
18.	20							0.0
19.	20	10				5	25	44.0
20.	16	10				5	25	44.0
21.	16	1.5						0.6
22.	16		2	2			5	4.5
23.	13	6	4			2	10	6.2
24.	13	3				1.5	15	5.8
25.	11							0.0
26.	11	3.5	1			1.5	10	6.9
27.	10							0.0
28.	10	2					10	8.1
29.	10							0.0
30.	9		6					1.6
31.	9		2	2				6.5
32.	9							0.0
33.	6							0.0
34.	6		1.5	1.5				5.0
35.	5							0.0
36.	5	3.5				0.7	3	9.2
37.	5							0.0
38.	3							0.0
39.	3							0.0
Totals	665	129.5	88.9	43.8	---	35.4	223	316.0

TABLE 6

SUMMARY OF CURRENT CAPABILITY
TO MANUFACTURE LOW-SULFUR (100 ppm) UNLEADED MOTOR GASOLINE

Current Capability to Manufacture Low-Sulfur Gasoline (%)	Number of Refineries by Category			Crude Capacity (MM b/d)	Estimated Low-Sulfur Unleaded Gasoline Capacity (MM b/d)
	100,000 b/d and over	30,000-99,999 b/d	under 30,000 b/d		
0	4	9	9	1.2	0
1-5	3	8	7	1.4	18
6-10	4	3	2	1.0	38
11-15	1	1	1	0.3	19
16-20	6	2	3	1.2	105
21-30	7	10	4	1.8	202
over 30	15	16	7	3.7	1,202
Sub-Total	40	49	33	10.6	1,584*
Unknown Capability	6	14	6	2.6	
Total	46	63	39	13.2	

* Equals about 30% of Total Gasoline Capacity of the 122 Refineries.

TABLE 7

SULFUR CONTENT (AVG. WT.%) IN CRUDE OIL AND GASOLINE
FOR REFINERIES WITH CAPACITY 100,000 b/d AND OVER

	Refinery Capacity	1974		1980	
		Crude	Gasoline	Crude	Gasoline
1.	{ Total capacity of 2.59 million * b/d for refineries larger than - 300,000 B/D	1.50	--	--	--
2.		1.00	.80	1.00	.065
3.		1.00	--	--	--
4.		.96	.066	.72	.0437
5.		.65	.05	1.00	.08-.12
6.		.48	.025	.90	.052
7.		.30	.025	.90	.03
8.	{ Total capacity of 2.21 million * b/d for refineries larger than - 200,000 B/D	1.00	.009	1.20	.0123
9.		1.00	.06	1.50	.06
10.		1.00	--	--	--
11.		1.00	.011	1.20	.013
12.		1.00	.05	2.00	.03
13.		.50	.04	.70	.04
14.		.50	.03-.04	1.30	.03-.04
15.		.40	.01	1.00	.015
16.		.30	.01	1.00	.016
17.	190	1.10	.005	1.10	.005
18.	190	1.50	.01	1.50	.01
19.	180	.30	.04	.35	.04
20.	180	1.40	.11	1.80	.12
21.	170	1.25	.005	1.50	.01
22.	170	.38	.013	.30	.013
23.	170	1.10	.07	.80	.07
24.	170	.20	.02	.20	.02
25.	170	.40	.024	1.00	--
26.	150	1.20	.06	2.00	.10
27.	150	.22	.013	1.70	.016
28.	140	.91	.06	1.32	.04
29.	140	1.10	.01	1.55	.01
30.	140	2.60	.04	2.00	.03
31.	130	.30	.021	.30	--
32.	130	.80	.04	.70	.04
33.	120	1.20	.07	1.20	.07
34.	120	.50	.01	1.00	.015
35.	120	.30	.02	--	--
36.	120	.60	.016	1.55	.01
37.	110	2.50	.03	2.50	.02
38.	110	.65	.035	.65	.035
39.	110	1.40	.10	1.40	.10
40.	110	1.00	.038	1.00	.038
41.	110	.50	.04	.70	.04
42.	100	.20	.04	1.30	.06
43.	100	1.60	.05	1.90	.01
44.	100	1.00	.026	1.20	.026
45.	100	.80	.009	1.20	.014
46.	100	.50	.02	.90	.02

*Refineries grouped together to maintain confidentiality of data.

TABLE 8

SULFUR CONTENT (AVG. WT.%) IN CRUDE OIL AND GASOLINE
FOR REFINERIES WITH CAPACITY 30,000-99,999 b/d

Refinery Capacity		1974		1980	
		Crude	Gasoline	Crude	Gasoline
1.	95	1.0	.005	1.0	.005
2.	95	1.2	.016	1.8	.023
3.	90	.50	.000	1.09	.01
4.	90	.20	.016	.20	--
5.	90	2.00	.05	3.0	.03
6.	90	.16	.012	.80	.033
7.	85	1.70	.10	2.0	.10
8.	85	.40	.02	--	--
9.	85	.70	.03	.7	.03
10.	85	.65	.03	1.0	.05
11.	85	.25	.02	.30	.02
12.	85	.25	.002	.50	.035
13.	85	1.25	--	--	--
14.	75	.55	.05	1.25	.05
15.	75	1.31	.035	1.20	.030
16.	70	.35	.016	.35	.016
17.	70	1.60	.06	1.60	.05
18.	70	1.00	.05	1.00	.03
19.	70	.25	.03	.85	.05
20.	70	.27	.042	.55	.028
21.	70	1.7	.015	1.5	.02
22.	65	2.0	.10	2.0	.01
23.	65	1.21	.23	1.30	.03
24.	65	.94	.016	.94	.016
25.	65	1.45	.025	1.45	.025
26.	65	.30	.035	.65	.032
27.	60	.20	.02	.25	.02
28.	60	1.40	.028	1.40	.028
29.	60	.20	.10	.80	.02
30.	55	.60	.02	--	--
31.	55	.06	.013	.11	--
32.	55	.40	.04	--	--
33.	55	1.5	.095	1.5	.095
34.	50	.93	.060	.83	.054
35.	50	.35	.02	.35	.02
36.	50	.65	.087	.65	--
37.	50	.75	.03	.75	.03
38.	50	.45	.030	.45	.035
39.	50	.30	.10	.30	.10
40.	50	.40	.02	.40	.02
41.	50	.47	.045	.58	.034
42.	45	1.2-1.7	.09-.096	1.2-1.7	.09-.096
43.	45	1.6	.06	1.8	.06
44.	45	.25	.025	.25	.025
45.	45	.50	.05	.50	.05
46.	45	.60	.025	.60	.025
47.	45	.50	--	--	--
48.	40	.82	.025	.80	.025
49.	40	1.0	.06	1.40	.015
50.	40	.90	.03	1.00	.04
51.	40	.28	.014	.28	.014
52.	40	.50	.03	1.15	.07
53.	40	.35	.025	.35	.025
54.	40	.20	.05	.45	.01
55.	40	1.7	.015	1.5	.02
56.	40	.50	.05	.50	.05
57.	35	.50	.02	1.50	.06
58.	35	.50	.03	1.50	.10
59.	35	1.02	.03	--	--
60.	35	1.0	.06	1.35	.08
61.	30	.75	.01	.75	.01
62.	30	.40	.02	--	--
63.	30	.80	.03	2.0	.045

TABLE 9

SULFUR CONTENT (AVG. WT.%) IN CRUDE OIL AND GASOLINE
FOR REFINERIES WITH CAPACITY UNDER 30,000 b/d

Refinery Capacity		1974		1980	
		Crude	Gasoline	Crude	Gasoline
1.	29	1.00	0.5	1.10	.05
2.	29	.30	.01	.30	.01
3.	29	1.00	.09	1.00	.09
4.	29	.62	.038	.86	.052
5.	27	.325	.019	.305	.019
6.	27	.15	.02	1.05	.02
7.	26	.70	.05	.70	.05
8.	26	1.70	.13	1.70	.10
9.	25	1.20	.12	1.50	.14
10.	25	.40	.032	.60	.04
11.	25	.50	.01	.50	.01
12.	23	.30	.03	--	--
13.	23	.60	.03	.50	.025
14.	22	.60	.01	.70	.005
15.	22	.645	.035	.645	.030
16.	21	.60	.03	.90	.05
17.	21	1.32	.034	1.32	.034
18.	20	.14	.01	.14	.01
19.	20	.28	.027	.74	.048
20.	16	.55	.032	.75	.042
21.	16	.08	0.1-0.2	--	--
22.	16	.28	.033	.50	.06
23.	13	.40	.023	.60	.03
24.	13	.50	.15	.50	.01
25.	11	.05	.01	.05	.01
26.	11	2.90	.17	2.90	.17
27.	10	.20	.002	.22	.002
28.	10	.30	.10	.30	.01
29.	10	.10	.008-.014	.10	.008-.014
30.	9	.015	.001	.020	.001
31.	9	.60	.025	--	--
32.	9	.08	.0001	.08	.0001
33.	6	.10	.008-.014	.10	.008-.014
34.	6	1.30	.90	1.30	.90
35.	5	.10	.008-.014	.10	.008-.014
36.	5	1.6	0.2	1.6	0.2
37.	5	.50	.03	.80	.04
38.	3	.10	.008-.014	.10	.008-.014
39.	3	.29	--	.25	--

PRODUCTION OF LOW-SULFUR GASOLINE

by

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July 1974

PART 1
PRODUCTION OF LOW-SULFUR GASOLINES
(PHASE 1)

CHAPTER 1

INTRODUCTION

This part of the report covers work which was performed under Contract No. 68-02-1308, Environmental Protection Agency, Office of Research and Monitoring, Task No. 10, Phase 1.

The crude mix used in Phase I resulted in capacities of the reformer, catalytic cracker and alkylation units which do not match the average U.S. refinery capacities. Future work planned for Phase II will modify the Phase I study in order to match the average U.S. production capacities of these units.

Future work planned for Phase III will be based on crudes and refinery capacities typical of the Los Angeles area.

Catalytic converters are to be installed in the exhaust systems of new cars starting with the 1975 model year. The use of catalytic converters is intended to control carbon monoxide and hydrocarbon emissions. However, the catalysts convert sulfur in the gasoline into sulfuric acid mists in the exhaust.

The purpose of this study is to determine the impact on oil refineries to produce unleaded, low-sulfur gasolines and also to desulfurize all gasolines produced for United States sales.

Prior to installation of additional desulfurization process units, unleaded, low-sulfur gasolines would have to be blended from existing low-sulfur gasoline blending stocks.

CHAPTER 2

SUMMARY

Automotive exhausts are to have catalytic mufflers for pollution control starting with the 1975 models. However, the catalysts convert the sulfur in gasoline into sulfuric acid mists in the exhaust.

This study indicates that the "typical" United States refinery can produce no-lead, low-sulfur gasoline blended from normal butane, alkylate and reformate. The predicted sales percent of no-lead and premium gasolines can be met for 1975 and 1976 with the total gasoline production meeting the EPA phase-down of lead antiknock additives. New desulfurization and octane upgrading facilities would have to be onstream by 1977 to produce the required sales percent of both no-lead, low-sulfur gasoline and premium gasoline.

The total gasolines could be made low sulfur by hydrodesulfurization of the gas oil feedstock to catalytic cracking and hydrodesulfurization of the light virgin and light thermal gasolines. Economics indicate that this scheme would add 0.74 cents per gallon to the cost of gasoline production.

An alternate case considers hydrodesulfurization of the catalytically cracked gasoline rather than the feedstock to the catalytic cracker. Economics indicate that use of this scheme to produce low-sulfur gasoline would add 0.95 cents per gallon to the cost of gasoline production. This cost includes a penalty of 0.33 cents per gallon debited to the lower octane resulting from partial hydrogenation of olefins in the FCC gasoline.

CHAPTER 3

DISCUSSION

GENERAL REFINERY SITUATIONS

No two crude oils or two refineries are the same. Furthermore, no two refineries will produce and have the same product demand. Depending upon the crude properties and refinery process capabilities, different refineries are geared to the following categories or combinations thereof:

Productions of gasolines, mid-distillates and residual oil.

Petrochemical production.

Lubricant production.

Asphalt production.

In crude topping and vacuum operations, crude oils can be distilled into fractions with true boiling cut points approximately as follows:

Butanes and lighter components to gas recovery.

Pentanes to 200° F light gasoline for blending to gasoline or isomerization of the pentanes and hexanes to upgrade the octane number.

200° F - 350° F naphtha for reformer feedstock to upgrade the octane number or produce aromatics.

350° F - 500° F kerosine for production of aviation jet turbine fuel and kerosine or for blending to diesel fuel or No. 2 fuel oil.

600° F - 1,000° F gas oil feedstock to catalytic cracking, thermal cracking or hydrocracking.

Heavier than 1,000° F residuum for blending No. 6 fuel oil or to asphalt or produced as feedstock for visbreaking, delayed coking, fluid coking or solvent deasphalting.

Typical ASTM distillations of refined products to sales are shown in Figure 1-1. Gasolines distill in the range of 80° F to 400° F, kerosine and jet fuel (kerosine-type) distill in the range of 340° F to 530° F, and diesel fuel and No. 2 fuel oil distill in the range of 350° F to 650° F.

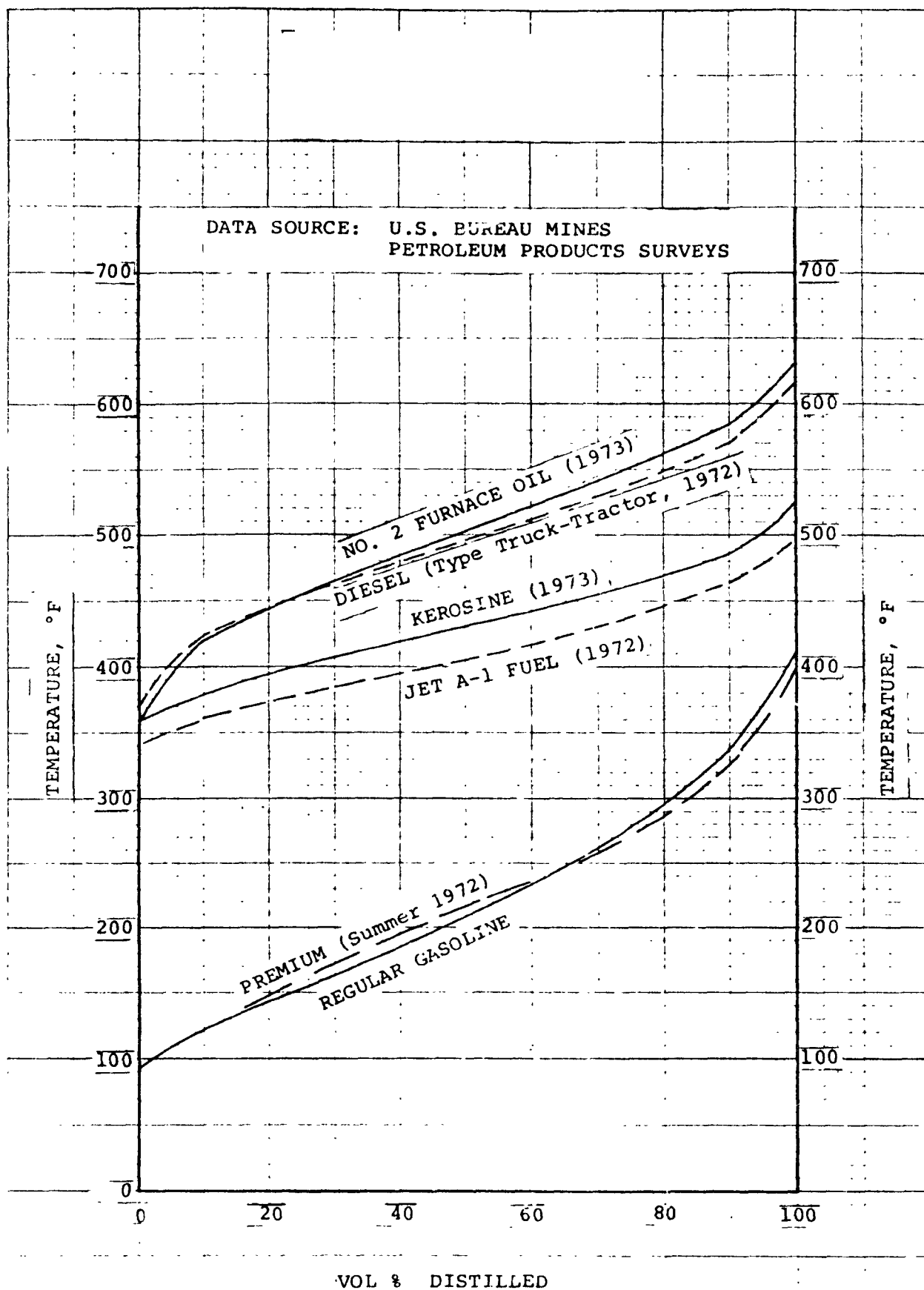


Figure 1-1. Typical ASTM distillations of petroleum products.

U.S. PRODUCTION OF PETROLEUM PRODUCTS

United States refineries produce petroleum products in relation to the market demands for quantities and properties.. Each refinery bases its operations on market demands and availability of crudes within the limitations of its refinery process units and the flexibility of operating conditions.

Table 1-1 shows the U.S. production of petroleum products in 1972. Table 1-2 shows the U.S. demand of mid-distillates by use in 1973. The term "mid-distillates" refers to the distillates boiling between gasoline and No. 6 fuel oil and comprises the kerosine, aviation jet fuel, diesel fuels and No. 2 heating oil. Kerosine, aviation jet fuel and No. 1-D diesel fuel are produced from the distillates boiling between 350 °F and 500° F true boiling cut points. No. 2 heating oil and No. 2-D diesel fuel are blends of essentially 50 percent of the 350 °F to 500° F fraction with 50 percent of the 500 °F to 600 °F fraction.

Table 1-3 shows typical properties of the petroleum products sold in the United States in 1972 and 1973.

It appears that the crude oils to supply needs in the United States above the domestic production will be supplied by the Persian Gulf countries. These crude oils have high sulfur contents and yield more residual fuel oil.

Therefore, it is expected that the sulfur content in the products will increase in the future unless additional desulfurization units are installed.

Table 1-1. U.S. PRODUCTION OF PETROLEUM PRODUCTS IN 1972

<u>Production</u>	<u>Million Barrels</u>	<u>Yield, %^a</u>	
Gasoline from Crude	2,014	47.0	
Natural Gas Liquids to Gasoline	305	7.1	
Gasoline Content of Naphtha-type Jet Fuel	38	0.9	
	<u>2,357</u>		<u>55.0</u>
Kerosine	80	1.9	
Kerosine-type Jet Fuel	233	5.4	
Kerosine Content of Naphtha-type Jet Fuel	38	0.9	
	<u>351</u>		<u>8.2</u>
Distillate Fuel Oil	964		22.6
Residual Fuel Oil	293		6.8
Lubricants	65		1.5
Losses	5		0.1
Unaccounted	552		12.9
Crude Runs to Stills Plus Natural Gas Liquids to Gasoline	<u>4,587</u>		<u>107.1</u>
<u>Refinery Input</u>	<u>Million Barrels</u>	<u>Input, %^a</u>	
Crude Runs to Stills	4,282	100.0	
Natural Gas Liquids to Gasoline	<u>305</u>	<u>7.1</u>	
	4,587	107.1	

^aVolume percent on crude input

Table 1-2. U.S. DEMAND FOR MID-DISTILLATES BY USE IN 1973

	<u>Million Barrels</u>	<u>%</u>
Kerosine	80	6.1
Kerosine-type Jet Fuel	233	17.6
Kerosine Content of Naphtha-type Jet Fuel	38	2.9
No. 1 Range Oil	<u>15</u>	1.1
	366	27.7
Diesel Fuel Used on Highways	164	12.4
Industrial Uses	50	3.8
Oil Company Fuel	14	1.1
Railroads	86	6.5
Vessel Bunkering	21	1.6
Military Uses	<u>17</u>	1.3
	352	26.7
Heating Oil	509	38.5
Gas and Electric Company Public Utility Power Plants	35	2.6
	544	41.1
Miscellaneous and Unaccounted	60	4.5
Total Mid-distillates	<u>1,322</u>	<u>100.0</u>

Table 1-3. TYPICAL PROPERTIES OF PETROLEUM PRODUCTS

	REGULAR GASOLINE	PREMIUM GASOLINE	REGULAR GASOLINE	PREMIUM GASOLINE	TOTAL GASOLINE POOL	AFROSINI	ILL. A-1 FUEL	DIESEL FUEL (TRUCKS)	NO. 2 FURNACE OIL	NO. 6 FUEL OIL
U.S. Bureau Mines Survey	Summer 1972	Summer 1972	Winter 1972-73	Winter 1972-73	Average 1972	1973	1972	1972	1973	197
Gravity, °API	60.5	60.7	62.5	63.0	61.7	42.3	42.4	36.5	35.1	31.0
Distillation ASTM °F										
IBP	92	91	84	84		341		37	37	
10%	122	123	108	109		378	36.2	42	43.5	
30	163	172	150	158						
50	208	217	200	209		428	40.5	40.5	40.4	
70	262	257	257	251		485	46.4	57.3	58.0	
90%	330	324	334	352		525		62.5	63.5	
EP	411	401	405	397						
Sulfur, wt %	0.047	0.026	0.038	0.023		0.067	0.065	0.21	0.22	1.80
Aniline Point, °F						146	140	147	143	
Cetane Number						166		27.1	27.1	17.0
Viscosity, CS at 100°F										
Viscosity, Furol at 122°F										
Carbon Residue, wt %										
Lead, g/gal	2.04	2.52	1.80	2.34						
Octane Number										
Research	94.1	99.8	93.9	99.6						
Motor	86.4	92.2	86.4	92.2						
(Research + Motor)/2	90.3	96.0	90.2	95.9						
Reid Vapor Pressure	9.2	9.3	12.2	12.1						
Total Gasoline Sales, %	38	62	37	63	0.031					
Sulfur, wt %	0.032			0.029	97.5					
Research Octane	97.6			97.5	90.0					
Motor Octane	90.0			90.1	93.8					
(Research + Motor)/2	93.8			93.8	2.24					
Lead, g/gal	2.34			2.14	10.7					
Reid Vapor Pressure										

UNLEADED GASOLINE

The Environmental Protection Agency has issued regulations (Jan. 10, 1973) on unleaded gasoline (minimum 91 research octane) to be supplied starting in July, 1974.

Unleaded gasoline to be used in automobiles equipped with catalytic converters is to be generally available in United States.

General Motors announced plans to equip all its 1975 models with converters, compared to about 60 percent for Ford. Thus about 80 percent of the 1975 automobiles will have catalytic converters.

Figure 1-2 shows predicted future sales percent of unleaded and premium gasolines.

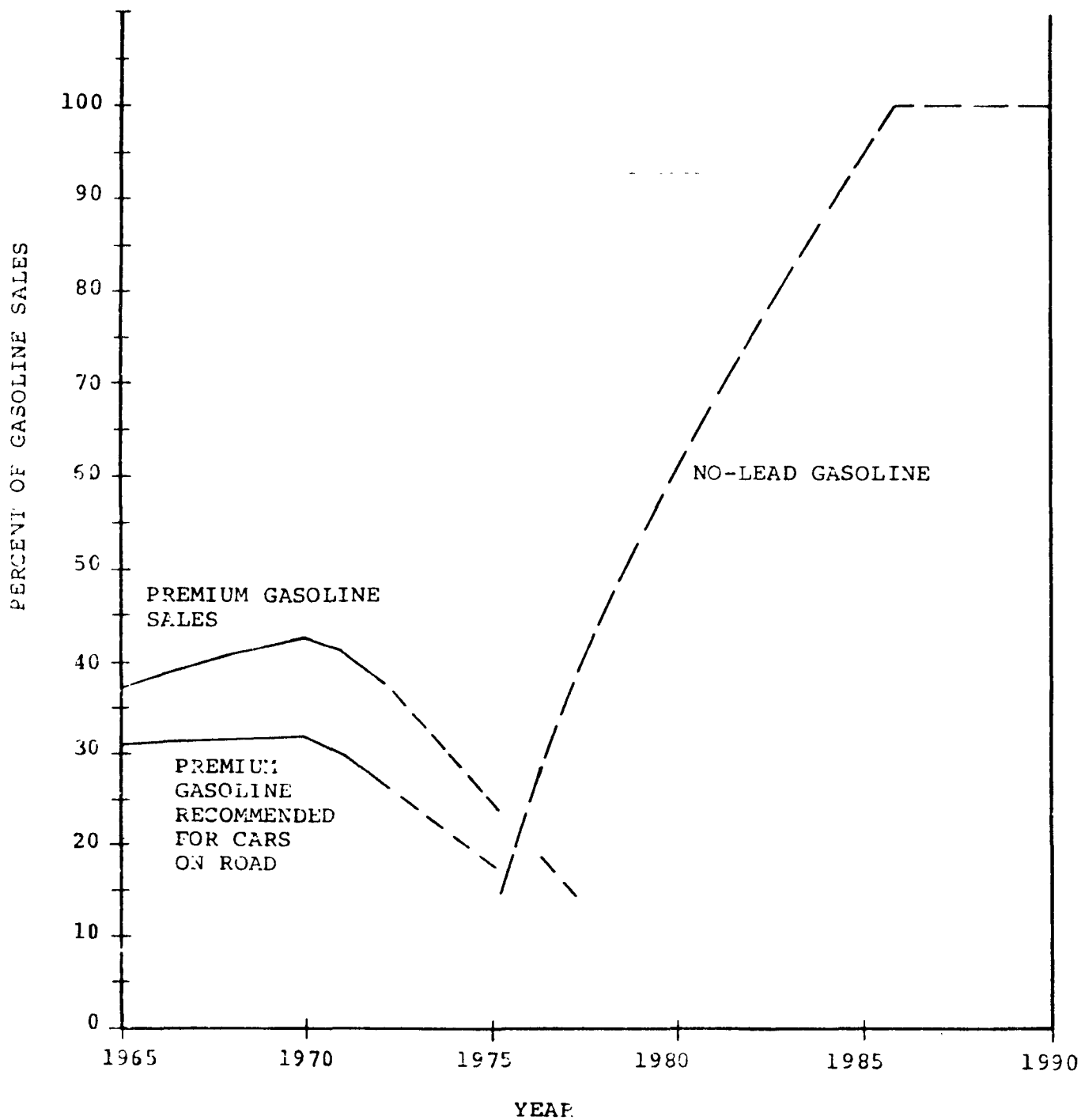


Figure 1-2. Projected percent of sales of premium and no-lead gasolines.

PHASE-DOWN OF LEAD IN GASOLINE

The Environmental Protection Agency has ordered a phased reduction of lead antiknock additives in gasoline (Federal Register, Dec. 6, 1973). These regulations restrict the average lead content in all grades of gasoline (including unleaded gasoline) produced by any refinery as follows:

<u>January 1</u>	<u>Lead Content Grams per Gallon</u>
1975	1.7
1976	1.4
1977	1.0
1978	0.8
1979	0.5

OCTANES OF TOTAL U. S. GASOLINES

The 1972 properties of the total U. S. gasoline pool were estimated from U. S. Bureau of Mines surveys and Ethyl Corporation sales data as follows:

Research Octane	97.5
Motor Octane	90.0
Lead, g/gal.	2.24
Sulfur, wt%	0.031

The response of lead content in the total U. S. gasoline pool was estimated from the lead response of various premium and regular gasoline blends. Figure 1-3 shows the research and motor octanes of the total U. S. gasoline pool in 1972 as a function of lead content.

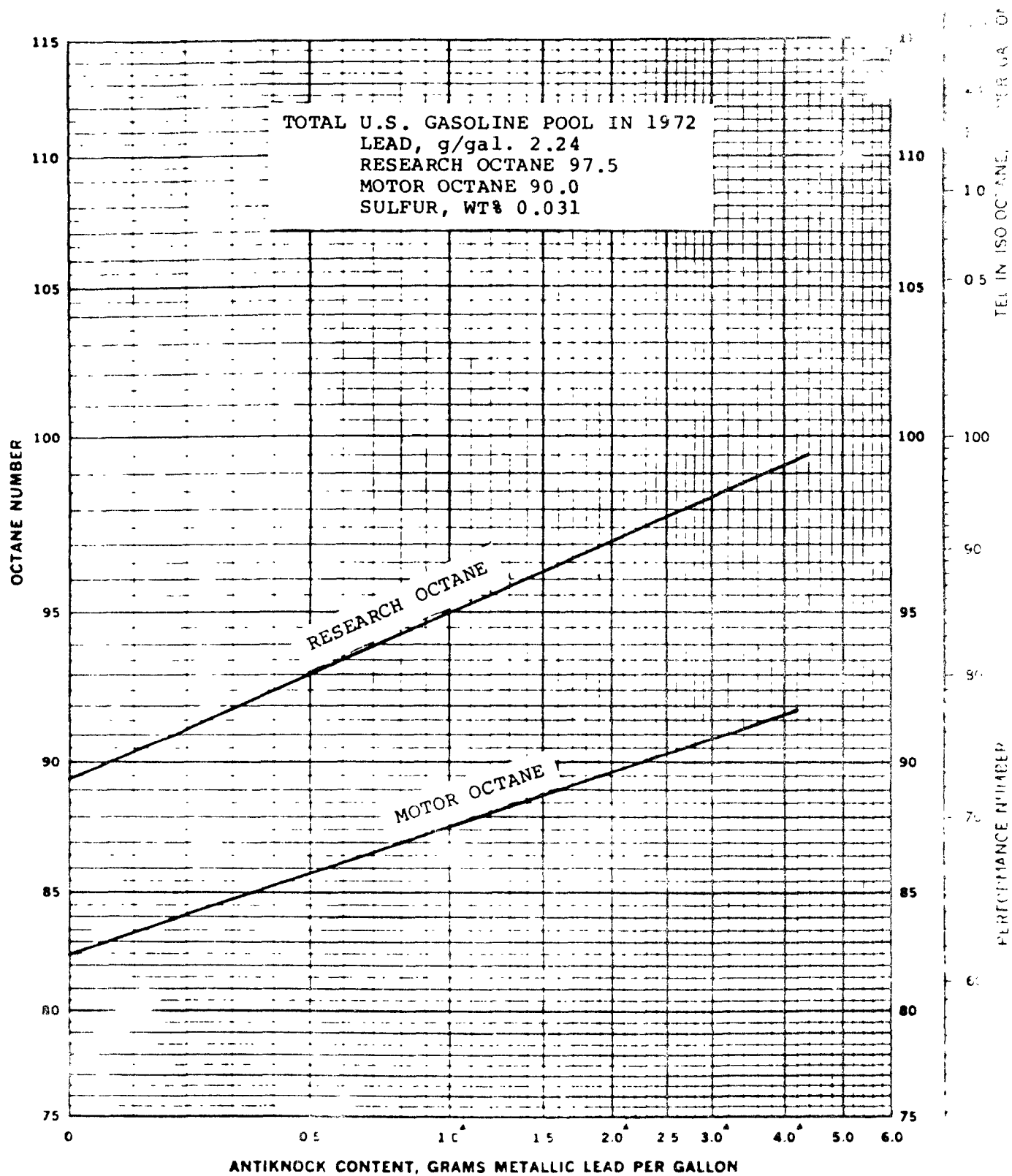


Figure 1-3. Octane of total U.S gasoline pool in 1972.

SULFUR IN GASOLINE BLENDING COMPONENTS

The sulfur contents of various light straight gasolines are shown in Table 1-4, and the sulfur contents in miscellaneous samples of other gasoline blending components are shown in Table 1-5.

The sulfur content is variable and depends upon the crude source for catalytically cracked gasoline, light straight-run gasoline, natural gasoline and coker or thermal gasoline.

Reformate and alkylate can be considered sulfur-free. The bi-metallic reformer catalyst requires that the feed naphtha be desulfurized to less than 1.0 ppm sulfur. The feedstocks to alkylation are desulfurized or essentially sulfur-free. In alkylation, the hydrofluoric acid catalyst or sulfuric acid catalyst quantitatively removes sulfur.

Therefore, production of sulfur-free gasoline generally will require the desulfurization of the thermally cracked gasoline, catalytically cracked gasoline and light straight-run gasoline.

Desulfurization of the gas oil feedstock to catalytic cracking will produce catalytically cracked gasoline with low sulfur content.

Table 1-4. SULFUR IN LIGHT VIRGIN GASOLINES*

<u>Crude Source</u>	<u>Sulfur, WT % In Light Gasoline</u>
East Texas	0.01
West Texas Intermediate Sweet	0.038
Ellenberger (Texas)	0.01
West Texas (0.31 wt % sulfur in crude)	0.01
West Texas Sour	0.15
Oklahoma City	0.011
Tinsley (Mississippi)	0.006
Corning (Ohio)	0.060
South Louisiana	0.006
Kuwait	0.006
Light Arabian (Saudi Arabia)	0.02
Light Iranian (Iran)	0.01

EC₅ - 200°F TBP

Table 1-5. SULFUR IN GASOLINE BLENDING COMPONENTS

<u>Gasoline Blending Components:</u>	<u>Sulfur, WT %</u>
Catalytically Cracked Gasoline	0.055 0.036 0.034 0.07 0.327 0.039 0.175
Alkylate	0.001 0.008 0.002 0.003
Catalytic Reformate	0.001 0.007 0.013 0.006 0.002
Coker Gasoline	0.089 0.19 1.43 0.59
Natural Gasoline	0.008 0.010 0.027

Analyses of miscellaneous samples

PRODUCTION OF NO-LEAD, LOW-SULFUR GASOLINE WITHOUT NEW FACILITIES

The time to plan, finance and construct refining facilities to upgrade gasoline blending components requires two to three years from the date of a firm decision to proceed.

During the period until the additional gasoline upgrade facilities are onstream, the no-lead, low-sulfur gasolines will have to be blended from low-sulfur components which can be produced in the present refining facilities.

The potential production of gasolines with the EPA phase-down of lead is shown in Table 1-6. Alkylate and reformate are the high-octane components and are components in both the unleaded and premium gasolines. The gasoline blends shown in Table 1-6 are based on the yields and properties from "A" Refinery (Case 1). The unleaded gasoline would be sulfur-free, since the blend consists of normal butane, alkylate and reformate. Comparison of the results in Table 1-6 with the projected percent of sales indicates that the present day refineries could produce the required sales percent of unleaded and premium gasolines in 1975 and 1976. New desulfurization and new octane upgrading facilities would have to be onstream by 1977 to produce the required sales percent of both no-lead, low-sulfur gasoline and premium gasoline.

Table 1-6. POTENTIAL GASOLINE PRODUCTION
WITH LEAD PHASE-DOWN (1)

<u>Year</u>	<u>1972</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>	<u>1978</u>	<u>1979</u>
<u>Lead Content, g/gal.</u>						
Allowed by EPA	4.2(2)	1.7	1.4	1.0	0.8	0.5
Total Gasoline Pool	2.2	1.3	1.3	0.7	0.7	0.65(3)
Premium Gasoline	2.4	2.5	3.0	3.0	-	-
Regular Gasoline	1.9	1.2	1.4	1.3	1.2	0.65
<u>Potential Gasoline, vol %</u>						
Unleaded (92 RON)	-	18	30	40	44	(3)
Premium (100 RON)	37	26	21	6	(3)	(3)
Regular (94 RON)	63	56	49	54	56	100
<u>Unleaded Gasoline, vol %</u>						None
N-Butane		14.2	14.2	14.2	14.2	
Alkylate		39.5	39.5	39.5	39.5	
Reformate		46.3	46.3	46.3	46.3	
<u>Premium Gasoline, vol %</u>					None	None
N-Butane		14.2	11.9	11.9		
Alkylate		39.5	25.5	25.5		
Reformate		46.3	29.4	29.4		
FCC Gasoline		-	33.2	33.2		
<u>Regular Gasoline, vol %</u>						
N-Butane		7.3	7.3	7.3	7.3	10.3
Light Virgin Gasoline		14.4	16.6	16.6	14.4	8.1
Light Coker Gasoline		2.0	2.4	2.4	2.0	1.2
FCC Gasoline		76.3	73.8	73.8	76.3	43.1
Alkylate						17.1
Reformate						20.2

(1)Based on gasoline yields and properties from "A" Refinery (Case 1).
Unleaded gasoline to be low-sulfur.

(2)Prior to EPA regulation.

(3)EPA regulation on lead content precludes production of unleaded and
premium gasolines if total gasoline pool requirements are to be met.

CHAPTER 4

DESULFURIZATION OF GASOLINE

CASE 1: TYPICAL "A" REFINERY

As a basis of comparison, a "typical" United States refinery and crude mix were selected to produce about the same distribution and properties of gasolines, mid-distillates and No. 6 fuel oil (Bunker "C") as the United States production in 1972.

The refinery feedstock was considered to be a 32 API crude oil containing 0.51 weight percent sulfur. For calculations, the crude mix was considered to be 90 percent South Louisiana and 10 percent Kuwait.

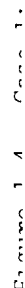
The refinery process units selected were as follows:

- Crude and Vacuum Distillation
- Catalytic Reformer with Hydrogen Pretreat Section
- Fluid Catalytic Cracker with Vapor Recovery
- Delayed Coker
- Alkylation
- Sulfur Recovery.

Figure 1-4 is a block flow diagram showing the yields and properties of the intermediate and final product streams. Case 1 is based on 100,000 barrels per calendar day (BPCD) of crude oil. Thus, the volume percent yields based on crude oil may be obtained by dividing the BPCD flows by 1,000. The sulfur from the crude oil is shown distributed in the product streams, recovered sulfur and emissions to the atmosphere.

Table 1-7 shows a comparison of the product yields and product properties for Case 1 with the 1972 U.S. production. The distribution of yields in Case 1 shows more gasolines and mid-distillates. This may be explained by the 13.4 percent unaccounted in the 1972 U.S. production. The properties of the products show general agreement between Case 1 and the 1972 U.S. production.

1. SULFONE COMPOUND SHOWN AS WITH AND W/O.
2. BAILING RANGES ARE TRUE BAILING CUT RANGES.
3. NET HEAT VALUE AT 6.1 MM BNG PER BARREL
FUEL OIL EQUIVALENT (H.C.E.).
4. GASOLINE OXIDIZER
RONIC RESERVOIR, CLEAR
ROM+300 APPROX 350 T.E.L.
NONE ABOVE, CLEAR
MOST 400 ABOVE 350 T.E.L.
5. RVP RED VINYL AROMATIC, P.S.I. AT 100°F



CL. ALKALINE
1783 BPCD 23.7 WPM
RVP 3.1 RMC 90.0 RMC 91.6
MWC 81.4 MWC 81.6

UNCONDENSED
N-BUTANE
4.4% BPCD
34.7% WPM

PROPANE LING
3.42 WPM
13.1% BPCD

UNCONDENSED
ISOBUTANE
3.75% BPCD
31.7% WPM

ALKYLATION
CL. ALKALINE
10.15 BPCD 71.7 WPM 103.0% RH
RVP 3.0 RMC 91.7 RMC 91.6
MWC 81.6 MWC 81.6

HEAVY OIL BUILDUP
190 WPM
1.5% BPCD
1.5% WPM

BPCD
CL 2.4%
IS 1.4%
CS 2.8%
CA 3.8%

TOTAL GASOLINE YIELD
58.83 BPCD 44.5 WPM
RVP 4.1 RVP 4.1
Sulfur: 0.03 WPM
OCTANE: 88.0
CLAR: 98.7
+ 2.3% LAMP 97.7
MWC 81.4

TOTAL GASOLINE YIELD
(OVERALL YIELD)
58.83 BPCD 44.5 WPM
RVP 4.1 RVP 4.1
Sulfur: 0.03 WPM
OCTANE: 88.0
CLAR: 98.7
+ 2.3% LAMP 97.7
MWC 81.4

VAPOR RECOVERY

WATER TREATING
+ SULFUR RECOVERY

GAS TO FUEL
23.7% WPM
MWC 81.6 RMC 91.6
2.3% BPCD 2.3% WPM

Sulfur
1.77% WPM
21.5% WPM/day

Sulfur
1.77% WPM
21.5% WPM/day

FCC GASOLINE
48.3% BPCD 38.1 WPM 375.4% WPM
Sulfur: 0.07 WPM 18.9 WPM
RVP 0.9 RMC 91.6 RMC 91.6
MWC 81.1 MWC 81.6

NO. 6 FUEL OIL (BUNKER C)

7.8% BPCD
13.4% WPM
RVP 0.6 RMC 91.6
MWC 81.1

CASE 2: "A" REFINERY WITH HYDRODESULFURIZATION OF CATALYTIC CRACKER FEED, LIGHT VIRGIN GASOLINE AND LIGHT COKER GASOLINE

In order to calculate the costs of producing sulfur-free gasoline, hydrodesulfurization of the gas oil feedstock to catalytic cracking and hydrodesulfurization of the light virgin and light coker gasolines were considered. In Case 1, the sulfur content in the light virgin gasoline would be 0.004 weight percent. The light virgin gasolines listed in Table 1-4 show higher sulfur content. Therefore, hydrodesulfurization of light virgin gasoline should be included in the "typical" refinery for cost purposes.

The refinery process units in Case 2 would be the same as in Case 1 with the following additions:

- Gas Oil Hydrodesulfurization
- Light Gasoline Hydrodesulfurization
- New Capacity for Amine Treating and Sulfur Recovery.

Figure 1-5 is a block flow diagram of Case 2 showing the yields and properties of the intermediate and final product streams. The yields and product properties also are listed in Table 1-7.

For gas oil desulfurization, the calculations are based on 80 percent sulfur removal with a hydrogen consumption of 42 standard cubic feet per pound sulfur removed (3.5 mols hydrogen consumed per mol sulfur removed). Above 85 percent sulfur removal, the hydrogen consumption increases due to saturation of polyaromatics and hydrocracking.

In Case 2, the hydrogen produced in the reformer would be more than adequate to supply the refinery needs.

The sulfur content would be 0.008 weight percent in the total gasolines.

Economics for producing low-sulfur gasoline in Case 2 are summarized in Table 1-8. Based on payout of the investment for the desulfurization units in five years (20 percent rate of return), the total added costs (above Case 1) would be about 0.74 cents per gallon of low-sulfur gasoline.

The economic basis is presented in the Appendix.

Table 1-9 shows the estimated investment for the desulfurization facilities in Case 2. Table 1-10 shows a comparison of yields in Case 1 and Case 2. Table 1-11 shows the estimated utilities and catalyst replacement cost in Case 2.

The apparent liquid gain in products over charges for Case 2 is 379 BPCD above Case 1. However, the utilities for the desulfurization facilities would require 584 BPCD of fuel equivalent. Thus, Case 2 would show a net loss of 205 BPCD in comparison to Case 1.

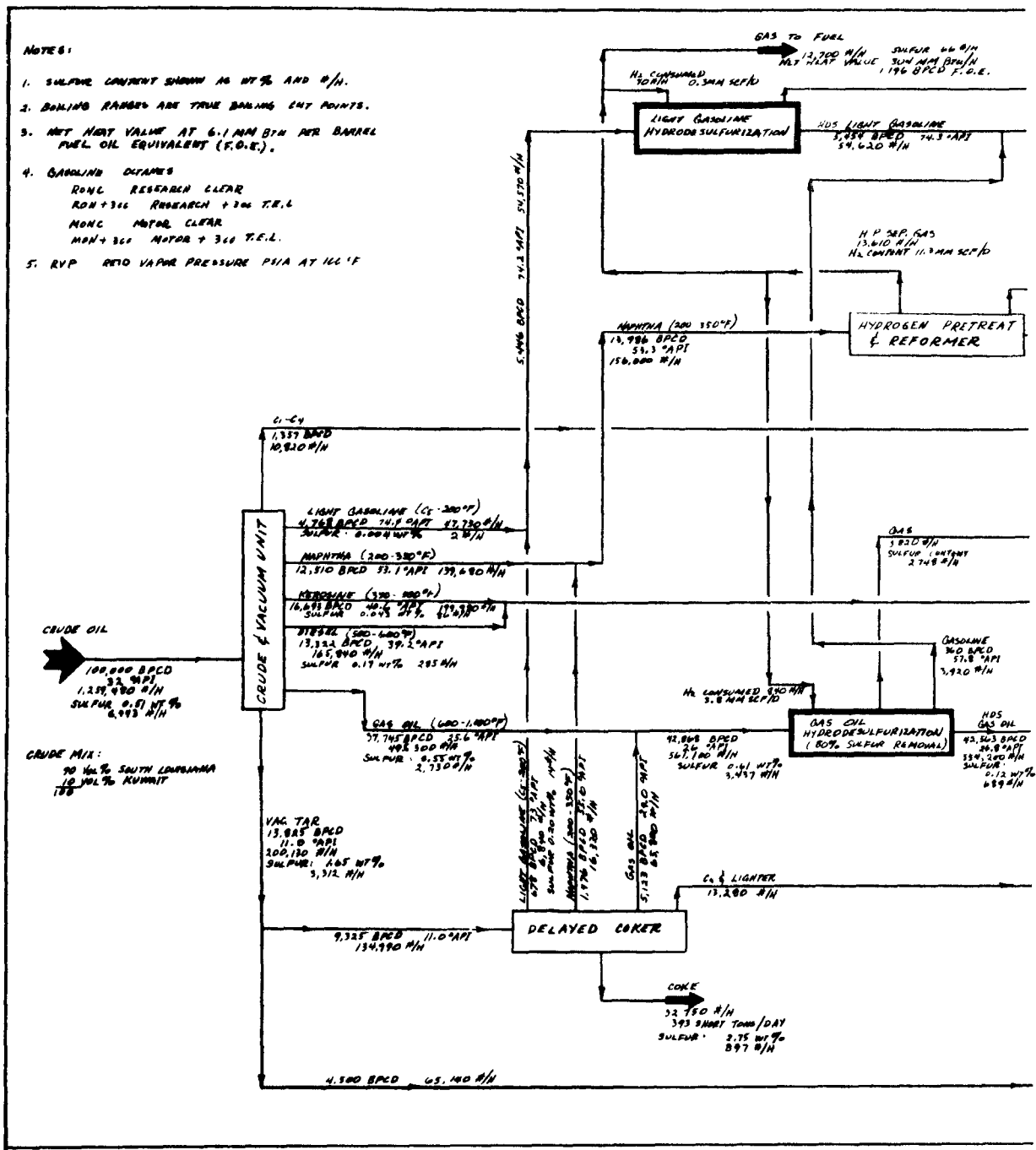
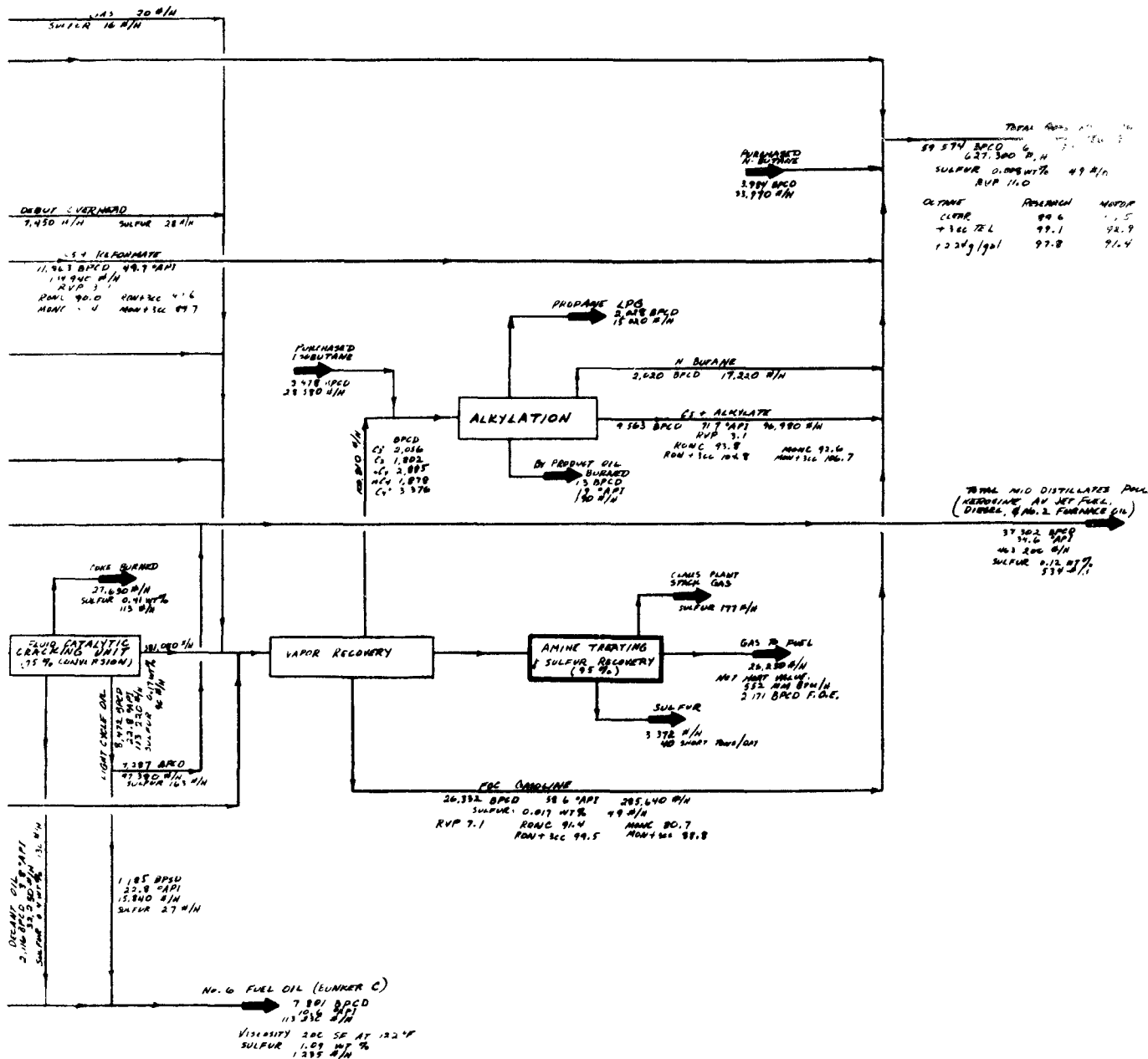


Figure 1-5. "A" refinery with hydrodesulfurization of cata-



lytic cracker feed, light virgin gasoline, and light coker gasoline.

Table 1-7. COMPARISON OF PRODUCTS

	1972 U.S. Production	Case 1	Case 2	Case 3
Total Gasolines				
Yield, vol %*	55.0	58.8	59.6	59.1
°API	61.7	64.2	64.3	64.8
Sulfur, wt %	0.031	0.033	0.008	0.007
Octanes:				
Research Clear		90.0	89.6	88.0
Research +3 cc		98.7	99.1	97.8
Motor Clear		82.9	82.5	82.1
Motor +3 cc		92.5	92.9	93.0
Research +2.24 g/gal.	97.5	97.7	97.8	96.7
Motor +2.24 g/gal.	90.0	91.4	91.4	91.8
Reid Vapor Pressure	10.7	11.0	11.0	11.0
Middle Distillates				
Yield, vol %*	30.8	37.6	37.3	37.6
Kerosine and Kerosine-type Jet Fuel				
Yield, vol %*	8.5	8.4	8.4	8.4
°API	42.3	41.0	41.0	41.0
Sulfur, wt %	0.066	0.041	0.041	0.041
Diesel Fuel				
Yield, vol %*	8.2	8.4	8.4	8.4
°API	36.5	37.3	37.3	37.3
Sulfur, wt %	0.21	0.19	0.19	0.19
No. 2 Furnace Oil				
Yield, vol %*	12.7	20.8	20.5	20.8
°API	35.1	30.5	31.0	30.5
Sulfur, wt %	0.22	0.31	0.11	0.31
No. 6 Fuel Oil				
Yield, vol %*	6.8	7.8	7.8	7.8
°API	11.0	10.0	10.6	10.0
Sulfur, wt %	1.6	1.5	1.1	1.5
Viscosity, Furol at 122°F	170	200	200	200
Carbon Residue, wt %	9.3	7.5	7.5	7.5
Miscellaneous Yield, vol %*				
Lubricants	1.5			
Delayed Coke (wt %)	13.4	2.6	2.6	2.6
Gas to Fuel (F.O.E.)		3.7	3.4	3.5
Unaccounted and Losses				

*Yield as volume percent of crude input

Table 1-8. COSTS FOR GASOLINE DESULFURIZATION - CASE 2*

Investment for Desulfurization Facilities	\$13.0 million
Years to Payout	5.0

	<u>Million Dollars per Year</u>	<u>\$/CD</u>
Cash Flow (13.0/5.0)	2.60	
Depreciation	0.87	
Net Profit	1.73	
Income Tax	1.73	
Gross Margin	3.46	
Operating Costs:		
Depreciation	0.87	
Operating Manpower	0.22	
Utilities	1.40	3,840
Catalyst Replacement	0.28	760
Interest	0.65	
Maintenance	0.46	
Local Taxes and Insurance	0.20	
Debit for Products		
(Case 1 - Case 2)	0.18	480
Credit for Lower Butane Charges	<u>(-0.94)</u>	<u>(-2,570)</u>
Total Operating Costs	3.32	
Total Added Cost for Low-sulfur Gasoline	6.78 (0.74 cents per gallon)	18,580

*Compared to Case 1

Table 1-9. INVESTMENT FOR PROCESS UNITS - CASE 2

<u>Process Unit</u>	<u>Capacity</u>	<u>Investment,¹ Million Dollars</u>
Light Gasoline Hydrodesulfurizer	5,700 BPSD	2.6
Gas Oil Hydrodesulfurizer	45,000 BPSD	6.5
Sulfur Recovery (Claus Plant)	Two 20 TPD Units	<u>0.9</u>
Onsite Subtotal		10.0
Offsite at 30 percent of Onsite		<u>3.0</u>
Total Investment		13.0

¹Investment includes paid-up royalty (if applicable) plus initial charge for catalyst.

Table 1-10. COMPARISON OF YIELDS - CASE 1 AND CASE 2

<u>CHARGES</u>	<u>BPCD</u>		<u>DIFFERENCE</u>
	<u>CASE 1</u>	<u>CASE 2</u>	
Crude Oil	100,000	100,000	-
Isobutane	3,864	3,478	(-386)
N-Butane	<u>4,065</u>	<u>3,984</u>	<u>(-81)</u>
Total Charges	107,929	107,462	(-467)
<u>PRODUCTS</u>			
Fuel Gas, F.O.E.	3,664	3,167	(-497)
Propane	2,047	2,028	(-19)
Gasolines	58,873	59,574	+701
Mid-distillates	37,592	37,302	(-290)
Sulfur	(21 TPD)	(40 TPD)	-
No. 6 Fuel Oil	7,784	7,801	+17
Delayed Coke	<u>(393 TPD)</u>	<u>(393 TPD)</u>	<u>-</u>
Total Product (Excluding Sulfur and Coke)	109,960	109,872	(-88)
Apparent Gain (Products - Charges)	2,031	2,410	+379

Table 1-11. UTILITIES AND CATALYST REPLACEMENT - CASE 2

Process Unit	Light Gasoline Hydrodesulfurization	Gas Oil Hydrodesulfurization	Sulfur Recovery	Total
			One 20 TPD Plant	
Consumption of Utilities:				
Electricity, kw	280	2,250	40	2,570
Fuel, MM Btu/hr	23.7	24.4	1.5	49.6
Cooling Water, gpm	380	2,400		2,780
Boiler Feedwater, lb/hr			5,250	5,250
Steam Consumed, lb/hr		58,000		58,000
Steam Generated, lb/hr			5,000	5,000
Net Steam Consumed, lb/hr				53,000
Cost of Utilities, \$/CD				3,840
Catalyst Replacement Cost, \$/CD	20	740		760
Fuel Equivalent of Utilities, BPCD (F.O.E.)				584

**CASE 3: "A" REFINERY WITH HYDRODESULFURIZATION OF LIGHT VIRGIN,
LIGHT COKER AND CATALYTICALLY CRACKED GASOLINES**

Case 3 considers the costs to produce sulfur-free gasoline by hydrodesulfurization of the catalytically cracked gasoline rather than the feedstock to the catalytic cracker.

The refinery process units in Case 3 would be the same as in Case 1 with the following additions:

FCC Gasoline Hydrodesulfurization
Light Gasoline Hydrodesulfurization.

Figure 1-6 is a block flow diagram of Case 3 showing the yields and properties of the intermediate and final product streams. The yields and product properties also are listed in Table 1-7.

Sulfur removal from the FCC gasoline was selected to yield about the same sulfur content in the total gasolines as in Case 2.

In Case 3, the sulfur removal would be 75 percent from the FCC gasoline. At this desulfurization severity, 42 percent of the olefins in FCC gasoline would be hydrogenated, which would result in decreased research octane.

Economics for producing low-sulfur gasoline in Case 3 are shown in Table 1-12. Based on payout of the investment for the desulfurization units in five years (20 percent rate of return), the total added costs (above Case 1) would be 0.95 cents per gallon of low-sulfur gasoline. The costs include a penalty of 0.33 cents per gallon debited to the lower octanes which result from partial hydrogenation of olefins in the FCC gasoline.

Table 1-13 shows the estimated investment for the desulfurization facilities in Case 3. Table 1-14 shows a comparison of yields in Case 1 and Case 2. Table 1-15 shows the estimated utilities and catalyst replacement.

The apparent gain (difference between products and charges) for Case 3 would be 38 BPCD above the apparent gain for Case 1. The utilities for the desulfurization facilities would require 594 BPCD of equivalent fuel oil. Thus Case 3 would result in a net loss of 556 BPCD compared to Case 1.

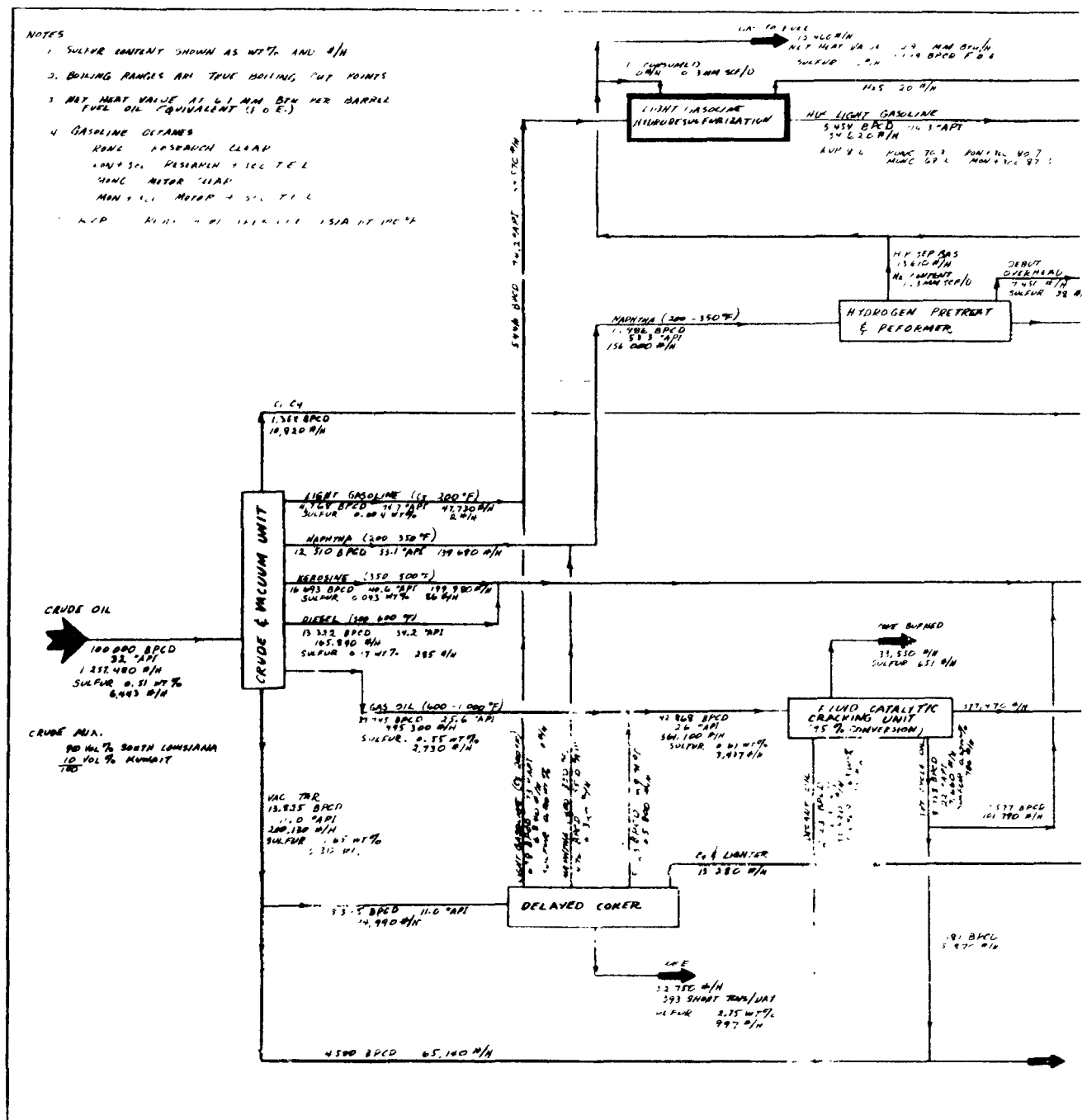
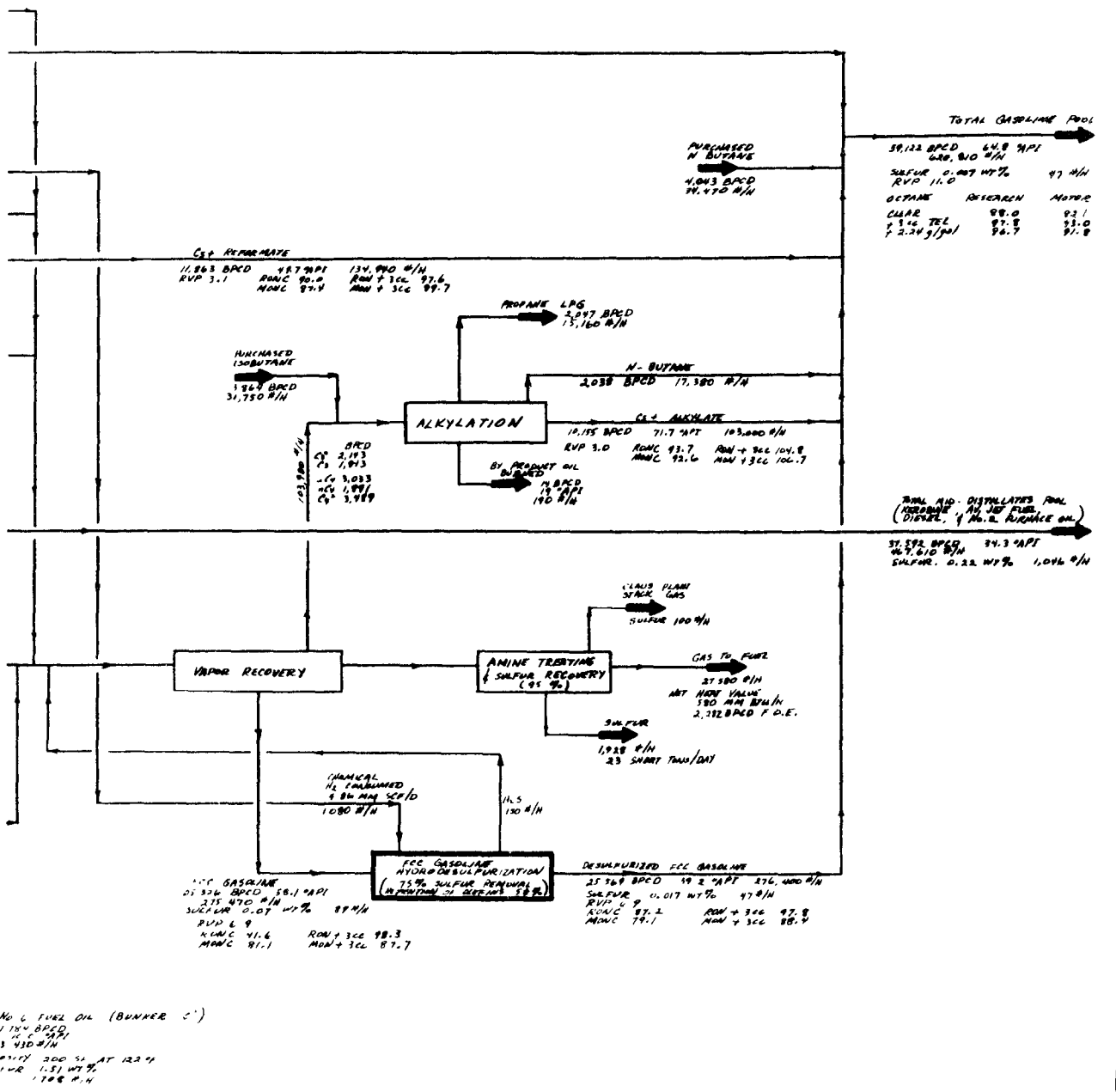


Figure 1-6. Case 3: "A" refinery with hydrosulfurization



of light virgin, light coker and FCC gasolines.

Table 1-12. COST FOR GASOLINE DESULFURIZATION - CASE 3*

Investment for Desulfurization Facilities	\$9.0 million
Years to Payout	5.0

	<u>Million Dollars per year</u>	<u>\$/CD</u>
Cash Flow (9.0/5.0)	1.80	
Depreciation	0.60	
Net Profit	1.20	
Income Tax	1.20	
Gross Margin	2.40	
Operating Costs:		
Depreciation	0.60	
Operating Manpower	0.22	
Utilities	1.43	3,920
Catalyst Replacement	0.04	100
Interest	0.45	
Maintenance	0.36	
Local Taxes and Insurance	0.14	
Debit for Lower Octane Gasoline	3.02	8,280
Credit for Lower Butane Charged	(-0.04)	(-120)
Credit for Products	(-0.03)	(-90)
Total Operating Costs	6.19	
Total Added Cost for Low-sulfur Gasoline	8.59	23,530
	(0.95 cents per gallon)	

*Compared to Case 1

Table 1-13. INVESTMENT FOR PROCESS UNITS - CASE 3

<u>Process Unit</u>	<u>Capacity</u>	<u>Investment, \$ Million Dollars</u>
Light Gasoline Hydrodesulfurizer	57,000 BPSD	2.6
FCC Gasoline Hydrodesulfurizer	26,700 BPSD	<u>4.3</u>
Onsite Subtotal		6.9
Offsite at 30 percent of Onsite		<u>2.1</u>
Total Investment		9.0

Investment includes paid-up royalty (if applicable) plus initial charge of catalyst.

Table 1-14: COMPARISON OF YIELDS - CASE 1 AND CASE 3

<u>CHARGES</u>	<u>BPCD</u>		<u>DIFFERENCE</u>
	<u>CASE 1</u>	<u>CASE 3</u>	
Crude Oil	100,000	100,000	-
Isobutane	3,864	3,864	-
N-Butane	<u>4,065</u>	<u>4,043</u>	<u>(-22)</u>
Total Charges	107,929	107,907	(-22)
<u>PRODUCTS</u>			
Fuel Gas, F.O.E.	3,664	3,431	(-233)
Propane LPG	2,047	2,047	-
Gasolines	58,873	59,122	+249
Mid-Distillates	37,592	37,592	-
Sulfur	(21 TPD)	(23 TPD)	-
No. 6 Fuel Oil	7,784	7,784	-
Delayed Coke	<u>(393 TPD)</u>	<u>(393 TPD)</u>	<u>-</u>
Total Product (Excluding Sulfur and Coke)	109,960	109,976	(+16)
Apparent Gain (Products - Charges)	2,031	2,069	+38

Table 1-15. UTILITIES AND CATALYST REPLACEMENT - CASE 3

Process Unit	Light Gasoline Hydrodesulfurization	FCC Gasoline Hydrodesulfurization	Total
Consumption of Utilities.			
Electricity, kw	280	1,320	1,600
Fuel, MM Btu/hr	23.7	111.1	134.8
Cooling Water, gpm	380	1,770	2,150
Cost of Utilities, \$/CD			3.920
Catalyst Replacement Cost, \$/CD	20	80	100
Fuel Equivalent of Utilities, BPCD (F.O.E.)			594

SULFUR DISTRIBUTION

Table 1-16 shows the sulfur distribution in the products and atmospheric emission as pounds per hour sulfur and as the percent of the sulfur in the crude charge.

The sulfur in gasoline is only a small fraction of the sulfur in the crude oil charge. The final combustion of the products used as fuel including gasolines, mid-distillates and Bunker "C" results in emissions of sulfur oxides to the atmosphere. The sulfur in delayed coke may be emitted to the atmosphere or be combined in metallurgical slag, depending upon the use of the delayed coke.

Table 1-16 shows that the recovered elemental sulfur would be 27.6 percent of the sulfur in the crude oil in a "typical" refinery (Case 1) and 52.3 percent of the sulfur in the crude oil in Case 2.

Table 1-16. SULFUR DISTRIBUTION

<u>Sulfur Content, LB/HR</u>	<u>Case 1</u>	<u>Case 2</u>	<u>Case 3</u>
Crude Oil	6,443	6,443	6,443
Products:			
Gasoline	205	49	47
Mid-distillates	1,046	534	1,046
Bunker "C"	1,708	1,235	1,708
Delayed Coke	897	897	897
Recovered Elemental Sulfur	1,776	3,372	1,928
Emitted as SO ₂ to Atmosphere	<u>811</u>	<u>356</u>	<u>817</u>
Total	6,443	6,443	6,443
<u>Sulfur Distribution, %</u>	<u>Case 1</u>	<u>Case 2</u>	<u>Case 3</u>
Products:			
Gasoline	3.2	0.8	0.7
Mid-distillates	16.2	8.3	16.2
Bunker "C"	26.5	19.2	26.5
Delayed Coke	13.9	13.9	13.9
Recovered Elemental Sulfur	27.6	52.3	30.0
Emitted as SO ₂ to Atmosphere	<u>12.6</u>	<u>5.5</u>	<u>12.7</u>
	100.0	100.0	100.0

* Sulfur distribution as percent of sulfur in crude charges.

APPENDIX A.

COSTS

1. All costs and capital are based on January, 1974 levels.
2. Capital related charges
 - Straight-line depreciation for 15 year life.
 - Interest at 10 percent per year. This is equivalent to 5 percent per year over the average payout period.
 - Maintenance: onsite, 4 percent; offsite, 2 percent.
 - Local taxes and insurance: 1.5 percent.
 - Payout on investment: 5 years after taxes.
3. U. S. income plus state corporation taxes at 50 percent of gross profit.
4. Incremental utility costs
 - Fuel: \$1.00 per million Btu net heat value. This is equivalent to \$5.50 per barrel of 32° API crude oil.
 - Electricity:

	\$ Per KWH
Fuel cost	<u>0.010</u>
Other charges	<u>0.006</u>
	0.016
 - Steam: \$1.40 per 1,000 pounds corresponding to the fuel cost of \$1.00 per million Btu.
 - Cooling water: \$0.02 per 1,000 gallons circulation.
 - Treated boiler feedwater: \$0.05 per 1,000 pounds.
5. Operating manpower costs
 - Average costs for stillman and operators at \$6.00 per hour plus 30 percent fringe benefits. Sixty percent overhead on operating manpower is added to allow for supervision, laboratory, technical service and instrument services.

5. Operating manpower costs (Contd.)

<u>Manpower Cost Per Shift Position</u>	<u>\$/HR</u>	<u>%</u>	<u>\$/YR</u>
Rate	6.00		52,600
Fringe Benefits		30	15,800
Overhead		60	<u>41,000</u>
Total			109,400

6. Product prices

Incremental product yields were priced at the same price as crude oil (\$5.50 per barrel).

7. Royalties

Gas oil hydrodesulfurization:

Paid-up royalty \$10.00 per BPCD feed rate.

Naphtha hydrodesulfurization:

Royalty-free. Royalty costs would be included in catalyst costs or nominal know-how fee.

8. Hydrogen make-up

Assumed to be available in the reformer make-gas for for hydrodesulfurization units.

9. Gasoline octane

Incremental gasoline octane priced at 2.0 cents per 6 octane difference between premium and regular gasolines at the 1972 lead level of 2.24 grams per gallon. This price is equivalent to 0.333 cents per gallon per research octane number.

APPENDIX B.

OIL EQUIVALENT OF UTILITIES

1. Fuel

Net heat value at 6.1 million Btu per barrel fuel oil equivalent.

2. Electricity

Net heat to generate electricity is assumed to be 10,000 Btu per kilowatt-hour. This requires 0.04 BPCD F.O.E. per kilowatt-hour.

3. Steam

Net heat to generate steam is assumed to be 1,370 Btu per pound of steam. This requires 5.4 BPCD F.O.E. per 1,000 pounds per hour of steam.

APPENDIX C.

SOURCES OF INFORMATION

American Petroleum Institute

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Industry Statistics, 1972 "

U. S. Bureau of Mines, Mineral Industry Surveys

"Motor Gasolines, Summer 1972"

"Motor Gasolines, Winter 1972-1973"

"Aviation Turbine Fuels, 1972"

"Diesel Fuels, 1973"

"Burner Fuel Oils, 1973"

U. S. Federal Register

Environmental Protection Agency

Part 80. Regulations of Fuels and Fuel Additives

Vol. 38, No. 6 - Jan. 10, 1973

Vol. 38, No. 234 - Dec. 6, 1973

Ethyl Corporation

"Yearly Report of Gasoline Sales by States, 1972"

Gulf Oil Corporation

"32.3° API Gravity South Louisiana Crude Oil (Ostrica Mix)"

"Kuwait Crude Oil Handbook"

PART 2
· PRODUCTION OF LOW-SULFUR GASOLINES
(PHASE 2)
CHAPTER 1

INTRODUCTION

This part of the report covers work which was performed under Contract No. 68-02-1308 for the Environmental Protection Agency, (EPA) Office of Research and Monitoring, Task No. 10, Phase 2.

Automobile manufacturers indicate that some automobiles will have catalytic mufflers for pollution control starting with the 1975 model year. To avoid poisoning of the catalyst, no-lead gasoline is required. The catalytic mufflers reduce emissions of carbon monoxide and hydrocarbons; however, the catalysts convert sulfur in the gasoline into sulfuric acid mist in the exhaust.

The purpose of this work is to determine the impact of producing low-sulfur gasolines on the refineries in the United States. To show the impact on U.S. refineries it was decided to select a "typical" refinery as a basis such that plant capacity, capacities of individual process units, yields of products, and properties of products about matches the average of the total U.S. refineries. Desulfurization facilities were then added to this refinery, using two process schemes, to produce low-sulfur gasolines.

The results presented herein supersede the results presented in the Phase I study.

CHAPTER 2

SUMMARY

This study shows how a "typical" U.S. refinery can produce no-lead, low-sulfur gasoline and by installing new hydrodesulfurization facilities produce the low sulfur gasolines to include the no-lead, premium and regular gasolines.

Results of this study indicate that no-lead, low-sulfur gasoline would have to be blended from normal butane, alkylate, and reformat in the existing "typical" United States refineries. Beyond 1975, the predicted demand of no-lead (low-sulfur) and premium gasolines could not be met with the EPA limits on lead anti-knocks in the total gasoline pools.

Total gasolines could be made low sulfur by hydrodesulfurization of the gas oil feedstock to catalytic cracking and by hydrodesulfurization of the light virgin and light coker (or thermal) gasolines. Economics for this scheme (Case 2) show that the costs for producing gasoline would be increased depending upon refinery size approximately as follows:

<u>Refinery Crude Capacity, BPCD</u>	<u>Desulfurization Costs, Cents Per Gallon</u>
16,000	1.59
44,000	1.01
100,000	0.67

An alternate case considers hydrodesulfurization of the catalytically cracked gasoline rather than the feedstock to the catalytic cracker. Economics indicate that this scheme (Case 3) to produce low-sulfur gasoline would add about 0.82 cents per gallon to the cost of gasoline pro-

duction for a 100,000 BPCD refinery. This cost includes a penalty of 0.3 cents per gallon of gasoline debited to the lower octane resulting from partial hydrogenation of olefins in the FCC gasoline.

If new facilities were installed to desulfurize all the U.S. gasolines by desulfurizing light virgin and thermal gasolines and desulfurizing the cat cracker feedstock, it would require an investment of about 2.0 billion dollars by U.S. refiners based on January, 1974 costs.

Based on the gasoline yields and properties in Case 2 for low-sulfur gasolines, no-lead, premium and regular gasolines could be blended in the predicted sales volumes and the total gasoline pool could meet the EPA regulations on lead phase-down until 1979. Octane up-grading would be required in 1979 to meet the limit of 0.5 grams of lead per gallon.

"A" Typical U.S. Refinery is shown as Case 1 and conforms to the following criteria:

- Median capacity of crude charges to U.S. refineries
- Capacities of process units within the refinery about matches the average percent of crude input as the total U.S. refineries.
- The crude charge produces about the average percent yields and properties of products as the total U.S. refineries.

CHAPTER 3

EPA REGULATIONS ON GASOLINES

UNLEADED GASOLINE

Regulations by the Environmental Protection Agency (EPA) to limit the emissions of carbon monoxide and hydrocarbons require most future automobiles to have catalytic mufflers.

General Motors announced plans to equip all its 1975 models with converters, compared to about 60 percent for Ford. Thus about 80 percent of the 1975 automobiles will have catalytic converters.

Unleaded gasoline to be used in automobiles equipped with catalytic converters is to be generally available in the United States at major service stations.

The EPA has issued regulations (January 10, 1973) on unleaded gasoline (minimum 91 research octane) to be supplied starting in July, 1974.

PHASE-DOWN OF LEAD IN GASOLINE

The EPA has ordered a phase reduction of lead anti-knock additives in gasoline (Federal Register, Dec. 6, 1973). These regulations restrict the average lead content in all grades of gasoline (including unleaded gasoline) produced by any refinery as follows:

<u>January 1</u>	<u>Lead Content Grams per Gallon</u>
1975	1.7
1976	1.4
1977	1.0
1978	0.8
1979	0.5

CHAPTER 4

PRODUCTION OF NO-LEAD, LOW-SULFUR GASOLINE IN PRESENT U.S. REFINERIES

DEFINITION OF "A" TYPICAL U.S. REFINERY

The purpose of this study is to determine the impact of producing low-sulfur gasolines by the refineries in the United States.

"A" Typical U.S. Refinery can be used to show the production of no-lead, low-sulfur in the present U.S. refineries and then develop the added costs to produce gasolines by installing new hydrodesulfurization facilities.

For this purpose, "A" Typical U.S. Refinery and the crude charge should conform to the following criteria:

- Median capacity of crude charges to U.S. refineries
- Capacities of process units within the refinery matches about the average percentage of crude input as the total U.S. refineries
- The crude charge produces about the average percent yields and properties of products as the total U.S. refineries

CASE 1: "A" TYPICAL U.S. REFINERY

The refinery process units selected for Case 1 were as follows:

- Crude and Vacuum Distillation
- Catalytic Reformer with Hydrogen Pretreat Section
- Fluid Catalytic Cracker with Vapor Recovery
- Delayed Coker

- Alkylation
- Sulfur Recovery

For calculations, the refinery feedstock was considered to be a 38.4° API mixture of Texas-Louisiana crude oils containing 0.5 weight percent sulfur.

Figure 2-1 is a block flow diagram showing the yields and properties of intermediate and final product streams. Case 1 is based on 100,000 barrels per calendar day (BPCD) of crude oil. Thus, the volume percent yields based on crude oil may be obtained by dividing the BPCD flows by 1,000. The vapor pressures and octanes of the gasoline component streams are shown in Figure 2-1. The sulfur in the crude oil is shown distributed in the product streams, recovered sulfur, and emissions to the atmosphere.

To simplify the work, the following conditions were assumed:

- Production of alkylate was set at 5.8 volume percent on crude input by taking propylene to LPG.
- Reformer would produce reformat with 95 research octane clear.
- Catalytic cracker would operate at 75% conversion with yields corresponding to riser cracking using zeolite catalyst.
- Unfinished asphalt would be produced from vacuum tar.
- Production of lubricants and waxes were not considered as these account for only 1.8 volume percent on crude input.

- Special naphthas and the benzene-toluene-xylenes aromatics were considered to be part of reformat and would be accounted in the total gasolines.

Comparisons of the results in Case 1 with the averages for the U.S. refineries from statistics are as follows:

- Table 2-1 - Comparison of Process Units in Case 1 with the U.S. Average
- Table 2-2 - Comparison of Products and Yields - 1972 U.S. Production vs. Typical Refineries.
- Figure 2-2 - Octane of Total Gasoline Pool - Typical Refineries

The median quantity of crude refined in the United States in 1973 was processed in refineries with a median capacity of about 100,000 barrels per stream day (BPSD) of crude oil. Capacities of refineries are usually expressed in barrels per stream or operating day (BPSD) whereas accounting of the annual production is on a barrels per calendar day (BPCD) which considers the down time.

These comparisons show that refinery and crude oil in Case 1 may be considered to be "A" Typical U.S. Refinery by conforming to the criteria stated previously in this chapter.

Further imports of foreign crudes with lower °API gravities, higher sulfur content, and higher metals content than domestic crudes will result in a somewhat different distribution of products with higher sulfur

NOTES:

1. "A" TYPICAL U.S. REFINERY:
Capacity of process units is about average percentage of crude input as the total U.S. refining capacity in 1973.
Product yields are about average percentage of crude input as total U.S. production in 1971 and 1972.
Properties of products are almost typical of average U.S. production in 1972 and 1973.
2. Boiling ranges are true boiling cut points.
3. Net heat value at 6.1 million Btu per barrel for 1 oil equivalent (F.O.D.).
4. GASOLINE OCTANES:
RONC RESEARCH OCTANE CLEAR.
RON + 3cc RESEARCH OCTANE PLUS 3cc T.E.L. Gal.
MONC MOTOR OCTANE CLEAR.
MON + 3cc MOTOR OCTANE PLUS 3cc T.E.L. Gal.
5. RVP REID VAPOR PRESSURE, PSI AT 100°F.
6. Sulfur content in streams shown as Wt% and in lb/H.

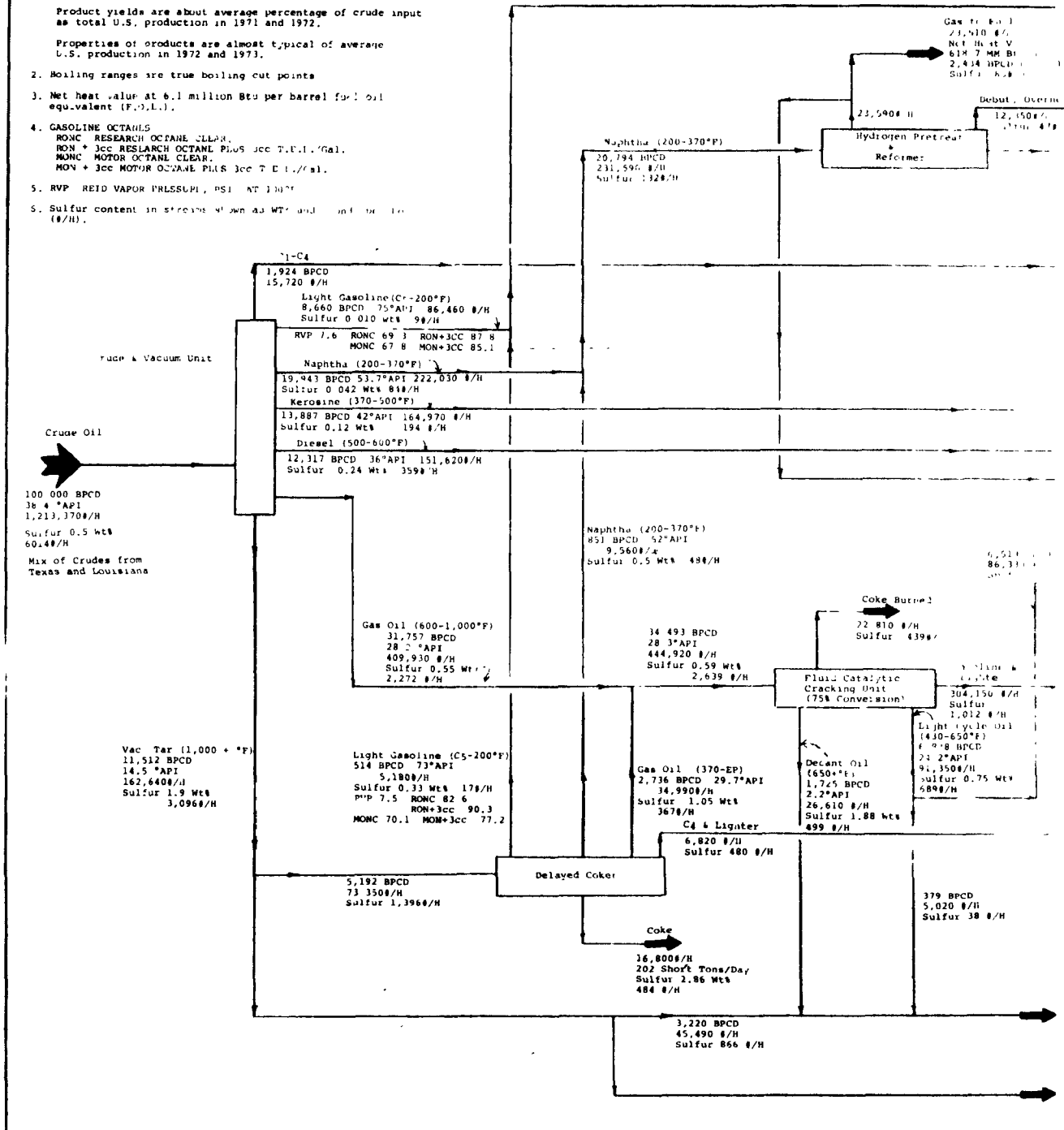
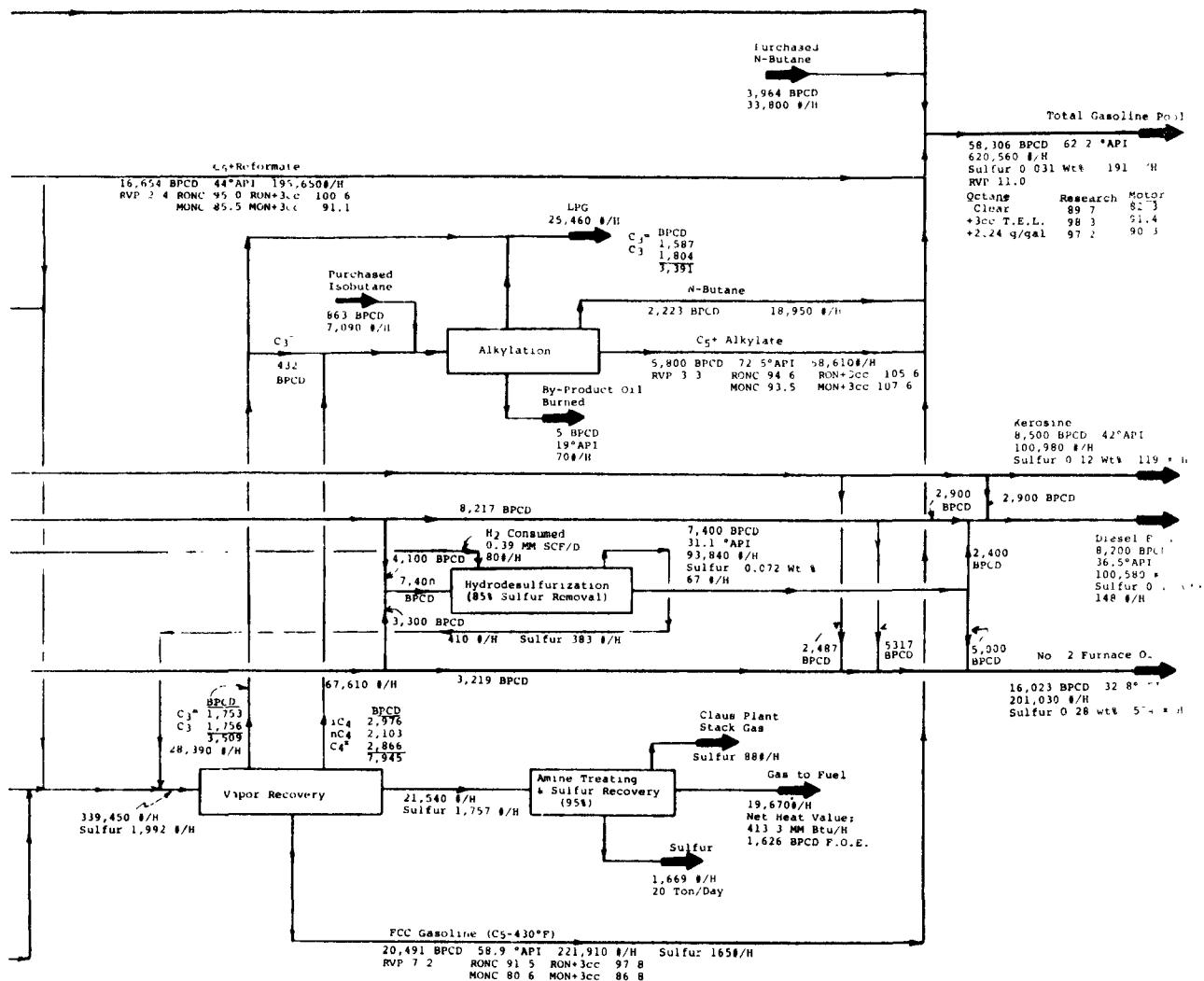


Figure 2-1. "A" typical



No. 6 Fuel Oil
 Bunker "C"
 5,324 BPCD
 10.9°API
 77,120 #/H
 Sulfur 1.82 Wt %
 1,403 #/H
 Viscosity 170 Furol Sec @ 122°F

Asphalt (Unfinished):
 3,100 BPCD
 14.5°API
 43,800 #/H
 Sulfur 1.9 Wt % 834 #/H

U.S. refinery (Case 1).

Table 2-1. COMPARISON OF PROCESS UNITS IN CASE 1
WITH THE U.S. AVERAGE

<u>Process Units</u>	<u>Vol. % of Crude Capacity</u>	
	<u>U.S. Refineries in 1973</u>	<u>Case 1</u>
Crude Distillation	100.0	100.0
Vacuum Distillation	36.8	37.8*
Cokers (Delayed and Fluid)	6.4	5.2
Catalytic Cracking	32.3	34.5
Naphtha Hydrodesulfurization	20.0	20.8
Catalytic Reformer	23.4	20.8
Mid-Distillate Hydrodesulfurization	7.9	7.4
Alkylation	5.8	5.8

* At 670°F TBP cut point in crude oil.

Table 2-2. COMPARISON OF PRODUCTS AND YIELDS,
1972 U.S. PRODUCTION VERSUS TYPICAL REFINERIES

<u>Total Gasolines</u>	<u>1972 U.S. Production</u>	<u>Case 1</u>	<u>Case 2</u>	<u>Case 3</u>
Yield, vol%	58.2	58.3	58.7	58.5
°API	61.7	62.0	62.1	62.6
Sulfur, wt%	0.031	0.031	0.006	0.006
Research Clear		89.7	89.3	88.0
Research + 3cc TEL		98.3	98.9	98.5
Research + 2.24 g. lead/gal	97.5	97.2	97.8	
Motor Clear		82.3	82.2	81.7
Motor + 3cc TEL		91.4	92.2	92.3
Motor + 2.24 g. lead/gal	90.0	90.3	91.1	
Reid Vapor Pressure	10.7	11.0	11.0	11.0
<u>Kerosine and Kerosine-Type Jet Fuel</u>				
Yield, vol%	8.5	8.5	8.5	8.5
°API	42.3	42.0	42.0	42.0
Sulfur, wt%	0.066	0.12	0.12	0.12
<u>Diesel Fuel</u>				
Yield, vol%	8.2	8.2	8.2	8.2
°API	36.5	36.5	36.5	36.5
Sulfur, wt%	0.21	0.15	0.13	0.15
<u>No. 2 Furnace Oil</u>				
Yield, vol%	14.4	16.0	15.7	16.0
°API	35.1	32.8	33.1	32.8
Sulfur, wt%	0.22	0.28	0.14	0.28
<u>No. 6 Fuel Oil</u>				
Yield, vol%	6.8	5.3	5.5	5.3
°API	11.0	10.9	12.6	10.9
Sulfur, wt%	1.6	1.8	1.3	1.8
Viscosity, Furol at 122°F	170	170	170	170
<u>Asphalt, vol% (5.5 bbl=1 short ton)</u>	3.8	3.1	3.1	3.1
<u>Coal, vol% (5 bbl=1 short ton)</u>	1.5	1.0	1.0	1.0

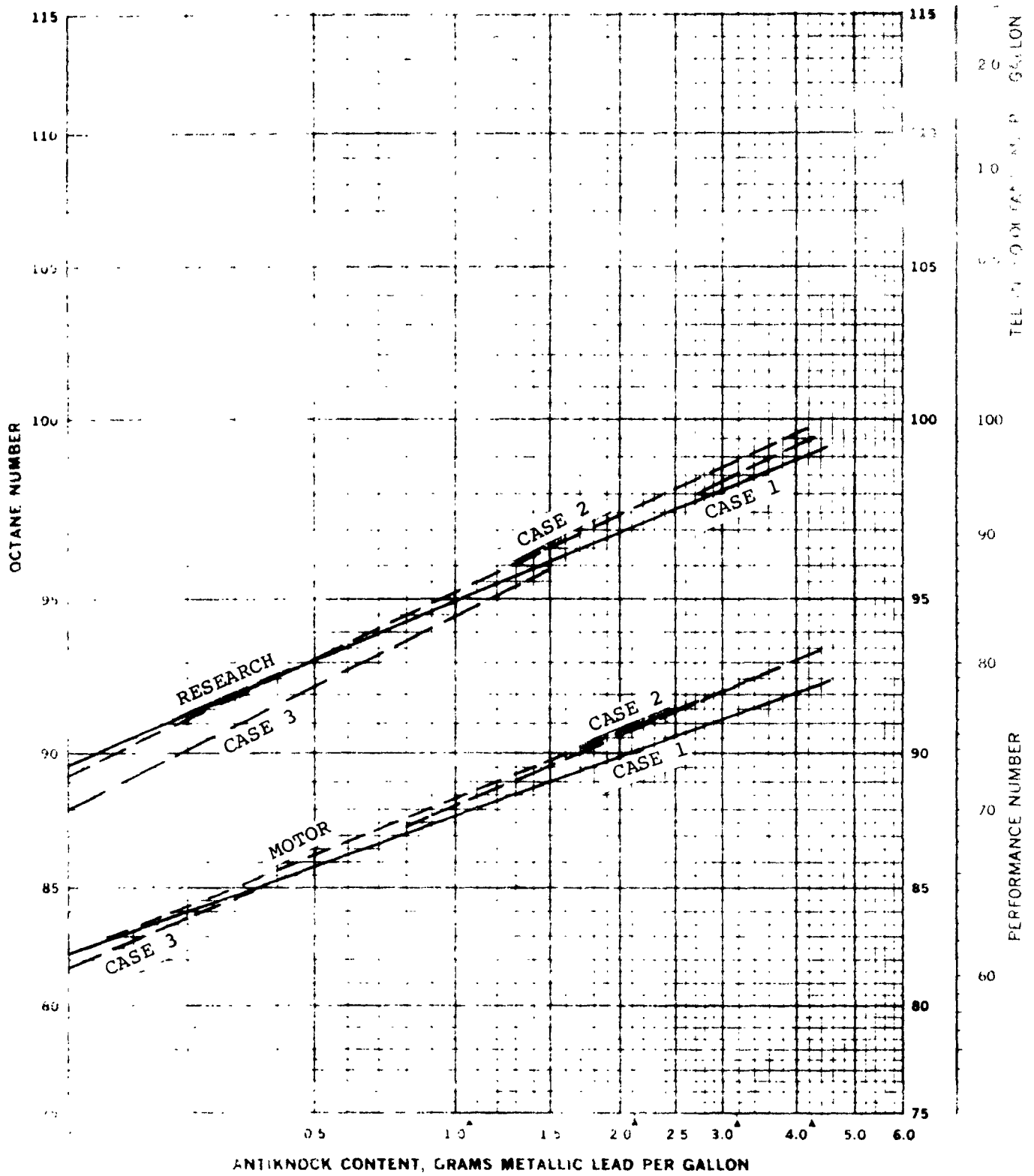
Table 2-2.(continued) COMPARISON OF PRODUCTS AND YIELDS,
1972 U.S. PRODUCTION VS. TYPICAL REFINERIES

	1972 U.S. <u>Production</u>	<u>Case 1</u>	<u>Case 2</u>	<u>Case 3</u>
<u>Liquefied Petroleum Gas (LPG), vol%</u>	1.9	3.4	3.7	3.4
<u>Still Gas to Fuel, vol%</u>	3.8	4.1	3.9	3.9
<u>Other Products, vol%</u>		None	None	None
Lubricants	1.6			
Wax (1 bbl-280 lb.)	0.2			
Road Oil	0.2			
Miscellaneous	0.3			

Notes:

1. Yields are volume percent on crude input.
2. Where 1972 yields were not available, they were estimated from 1971 products. Petrochemical feedstocks (aromatics) and special naphthas added into total gasoline production.

LEAD ALKYL ANTIKNOCK SUSCEPTIBILITY CHART



Correlation of octane number to 10, 20, 30 and 40 mi/l/gallon

Figure 2-2. Octanes of total gasoline pool.

content than shown in Case 1.

PRODUCTION OF NO-LEAD, LOW-SULFUR GASOLINE IN PRE-SENT FACILITIES

The time to plan, finance and construct refining facilities to upgrade gasoline blending components requires two to three years from the date of a firm decision to proceed. During the period until the additional gasoline-upgrade facilities are onstream, the no-lead, low-sulfur gasolines will have to be blended from low-sulfur components which can be produced in the present refining facilities.

Sulfur contents of various gasoline blending components can be shown by the analyses of various samples in Tables 2-3 and 2-4. The sulfur content is variable and depends upon the crude source for catalytically cracked gasoline, light straight-run gasoline, natural gasoline and coker or thermal gasoline.

Reformate and alkylate can be considered sulfur-free. The bi metallic reformer catalysts require that the feed naphtha be desulfurized to less than 1.0 ppm sulfur. The feedstocks to alkylation are desulfurized or essentially sulfur-free. In alkylation, the hydrofluoric acid catalyst or sulfuric acid catalyst quantitatively removes any residual sulfur.

Production of sulfur-free gasolines generally will require the desulfurization of thermally cracked gasoline, catalytically cracked gasoline, and light straight-run gasoline. However, until new desulfurization facilities are installed, the requirements for no-lead, low-sulfur

Table 2-3. SULFUR IN GASOLINE BLENDING COMPONENTS

<u>Gasoline Blending Components*</u>	<u>Sulfur, WT%</u>
Catalytically Cracked Gasoline	0.055 0.036 0.034 0.07 0.327 0.039 0.175
Alkylate	0.001 0.008 0.002 0.003
Catalytic Reformate	0.001 0.007 0.013 0.006 0.002
Coker Gasoline	0.089 0.19 1.43 0.59
Natural Gasoline	0.008 0.010 0.027

*Analyses of miscellaneous samples

Table 2-4. SULFUR IN LIGHT VIRGIN GASOLINES*

<u>Crude Source</u>	<u>Sulfur, WT% In Light Gasoline*</u>
East Texas	0.01
West Texas Intermediate Sweet	0.038
Ellenberger (Texas)	0.01
West Texas (0.31 wt% sulfur in crude)	0.01
West Texas Sour	0.15
Oklahoma City	0.011
Tinsley (Mississippi)	0.006
Corning (Ohio)	0.006
South Louisiana	0.006
Kuwait	0.006
Light Arabian (Saudi Arabia)	0.02
Light Iranian (Iran)	0.01

*C₅ - 200°F TBP

gasolines will have to be blended from low-sulfur blend stocks, such as n-butane, reformat and alkylate.

Starting in July, 1974 the no-lead gasoline will have to be available for the 1975 automobiles equipped with catalytic mufflers. Gasoline blending components presently available will be used to blend the no-lead, premium, and regular gasolines. In future years as more automobiles in service have catalytic mufflers and the pre-1971 automobiles are increasingly junked, more no-lead gasoline and less premium gasoline will be required to satisfy automobile needs. The 1971 and later automobiles without catalytic mufflers can use regular gasoline.

Figure 2-3 shows a projected percent of sales of premium and no-lead gasolines.

The potential production of no-lead, low-sulfur gasoline together with premium and regular gasolines was calculated attempting to meet the EPA regulations on lead phase-down using the blending components produced in Case 1. These results (Table 2-5) indicate that the projected percent of gasoline sales can be produced through 1975. In 1976 and later years the EPA limit on lead content would be exceeded. In 1977 and later years the production of no-lead, low-sulfur and premium gasolines would be less than the projected percent of sales.

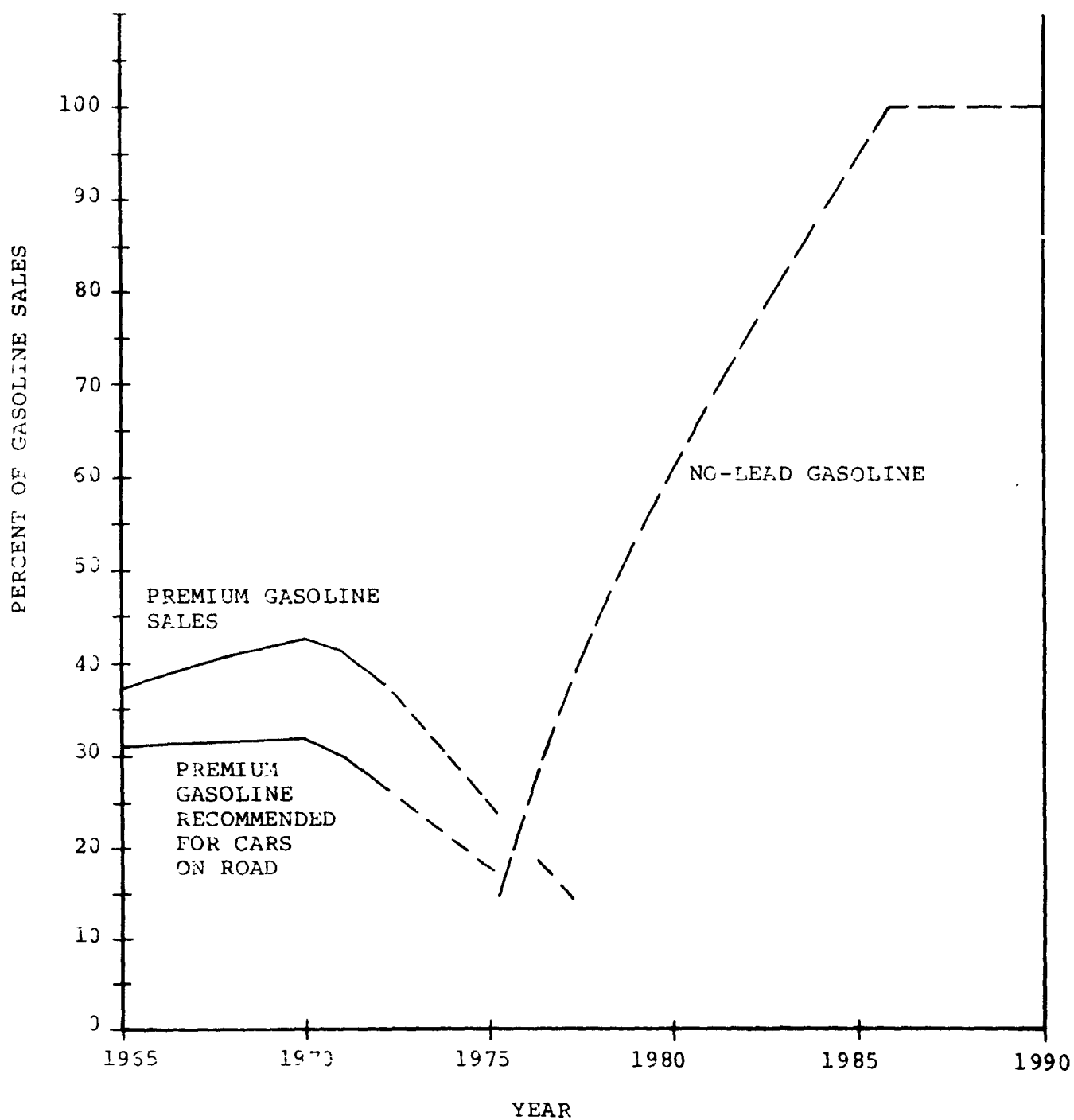


Figure 2-3. Projected percent of sales of premium and no-lead gasolines.

Table 2-5. POTENTIAL GASOLINE PRODUCTION IN CASE 1⁽¹⁾
WITH LEAD PHASE-DOWN

Year	<u>1972</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>	<u>1978</u>	<u>1979</u>
<u>Lead Content, g./gal</u>						
Allowed by EPA	4.2 ⁽²⁾	1.7	1.4	1.0	0.8	0.5
Total Gasoline Pool		1.6	1.55	1.5	1.3	1.3
Premium Gasoline		1.8	2.6	3.0	-	-
Regular Gasoline		2.0	2.1	2.4	2.3	2.3
<u>Potential Gasoline, vol%</u>						
No-Lead, Low Sulfur		18	30	40	45	45
Premium (100 RON)	37	23	16	9	None	None
Regular (94 RON)	63	59	54	51	55	55
<u>No-Lead Gasoline, vol%</u>						
N-Butane		15	15	15	15	15
Alkylate		22	22	22	22	22
Reformate		63	63	63	63	63
<u>Premium Gasoline, vol%</u>						
					None	None
N-Butane		15	13	12		
Alkylate		22	15	12		
Reformate		63	44	35		
FCC Gasoline			28	41		
<u>Regular Gasoline, vol%</u>						
N-Butane		8	8	7	7	7
Light Virgin Gasoline		25	27	29	27	27
Light Coker Gasoline		2	2	2	2	2
FCC Gasoline		59	57	61	64	64
Alkylate		1	1	-	-	-
Reformate		5	5	1	-	-
<u>Gasoline Octanes</u>						
No-Lead, Research		94.7	94.7	94.7	94.7	94.7
Motor		87.9	87.9	87.9	87.9	87.9
Premium, Research	99.7	100.2	100.2	100.2		
Motor	92.2	94.8	93.3	92.6		
Regular, Research	94.0	94.2	94.2	94.2	94.2	94.2
Motor	86.4	86.3	87.0	86.3	86.2	86.2
Comment - See Note			3.	4.	5.	6.

Notes on Table 2-5:

- (1) Potential gasoline blends are based on the gasoline yields and properties from "A" Typical U.S. Refinery (Case 1). The no-lead, low-sulfur gasoline would be blended from normal butane, alkylate, and reformate.
- (2) Legal limit was 4.2 grams lead content per gallon prior to EPA regulations.
- (3) Predicated sales demand of premium gasoline and no-lead, low-sulfur gasoline precludes meeting the EPA limit on lead content in 1976.
- (4) Predicated sales demand of no-lead, low-sulfur gasoline reduces the production of premium gasoline below predicted sales demand. Lead content in total gasoline pool exceeds EPA regulation in 1977.
- (5) In 1978 and 1979, the octanes of the gasoline components limits the production of no-lead, low-sulfur gasoline below predicted sales demand. The production of no-lead, low-sulfur gasoline precludes the production of premium gasoline. The lead content in the total gasoline pool exceeds the EPA regulation in 1978 and 1979.

CHAPTER 5

DESULFURIZATION OF GASOLINE

CASE 2: "A" REFINERY WITH HYDRODESULFURIZATION OF CATALYTIC CRACKER FEED AND LIGHT GASOLINES

In order to calculate the costs of producing low-sulfur gasolines, hydrodesulfurization of the gas oil feedstock to catalytic cracking and hydrodesulfurization of the light virgin and light coker gasolines were considered.

In Case 1, the sulfur content in the light virgin gasoline is 0.01 wt.%. However, hydrodesulfurization of light virgin gasoline should be included for the "typical" refinery for cost purposes because some of these gasolines, as shown in Table IV, have high sulfur contents.

In Case 2, the refinery process units would be same as in Case 1 of "A" Typical U.S. Refinery with the following additions:

- Gas Oil Hydrodesulfurization
- Light Gasoline Hydrodesulfurization
- New Capacity for Amine Treating and Sulfur Recovery

Figure 2-4 is a block flow diagram of Case 2 showing the yields and properties of the intermediate and final product streams. The yields and product properties are listed in Table 2-2 together with the average U.S. production.

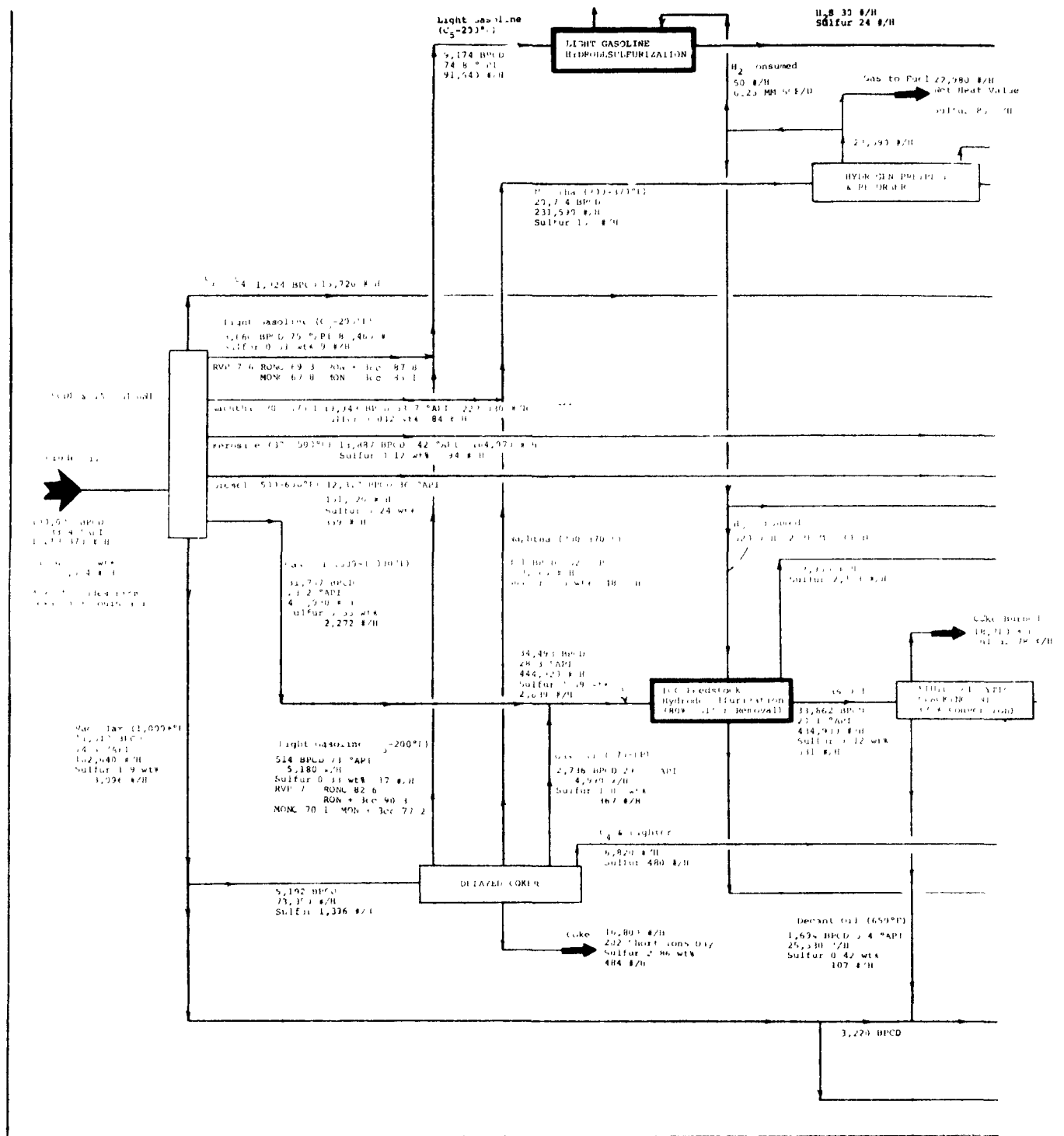
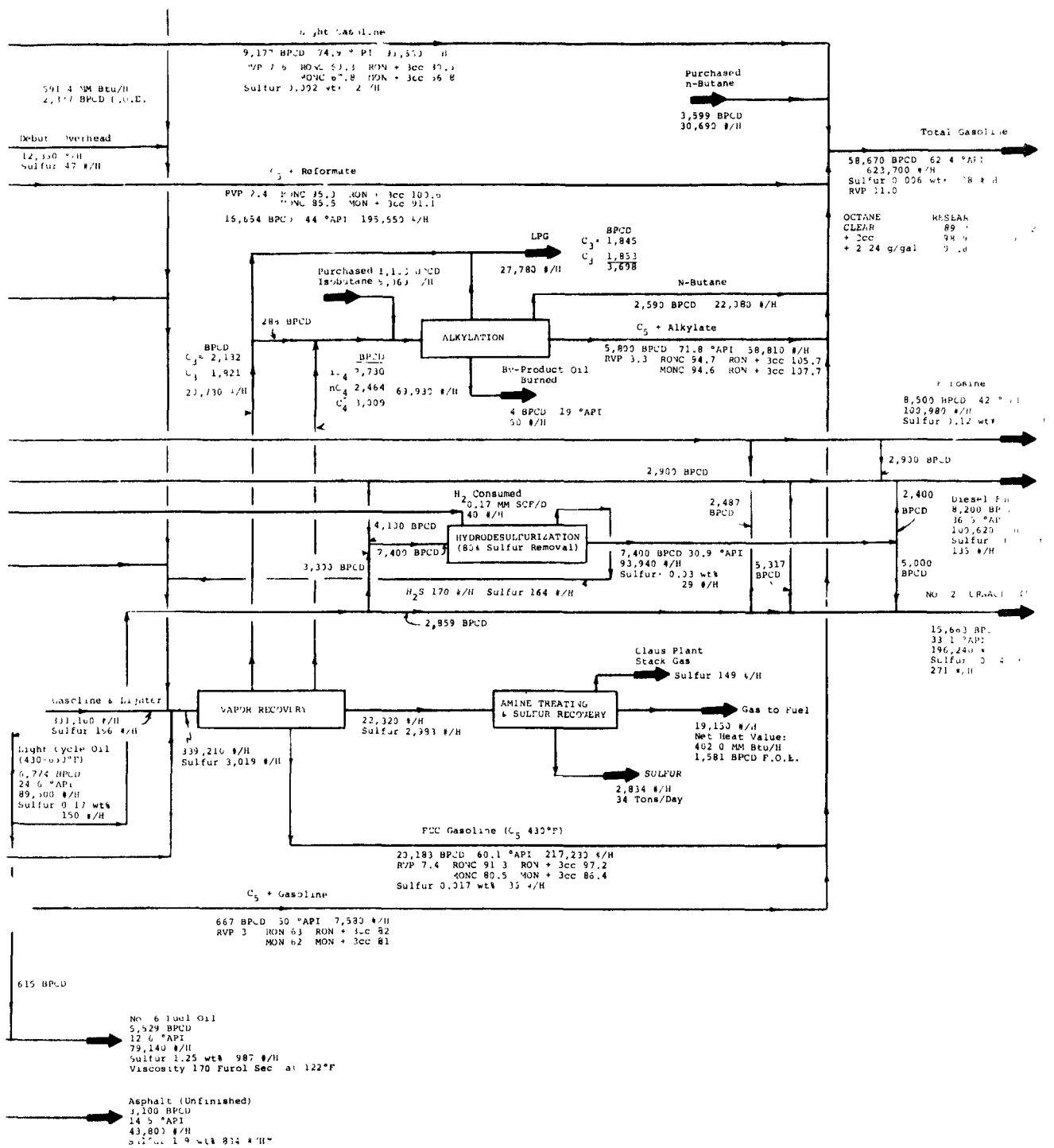


Figure 2-4. "A" typical U.S. refinery with hydrodesulfuriza-



tion of cal. cracker feed and light gasolines.

For desulfurization of the gas oil, the calculations are based on 80 percent sulfur removal with a hydrogen consumption of 42 standard cubic feet per pound sulfur removed (3.5 mols hydrogen consumed per mol sulfur removed). Above 85 percent sulfur removal, the hydrogen consumption increases due to saturation of polyaromatics and hydrocracking.

In Case 2, the hydrogen produced in the reformer would be more than adequate to supply the refinery needs. The sulfur content would be 0.008 weight percent in the total gasolines.

Economics for producing low-sulfur gasoline in Case 2 are summarized in Table 2-6 and estimated investments for the desulfurization facilities are shown in Table 2-7. The economic basis is presented in the Appendix. The investment for the desulfurization facilities is assumed to pay out in five years (20 percent rate of return.)

The total added costs to produce low-sulfur gasolines (above Case 1) depends upon refinery size as follows:

<u>Refinery Capacity, BPCD</u>	<u>Added Costs to Produce Low-Sulfur Gasoline, Cents Per Gallon</u>
16,000	1.59
44,000	1.01
100,000	0.67

Table 2-8 shows a comparison of yields in Case 1 and Case 2. Table 2-9 shows the estimated

Table 2-6. COSTS FOR GASOLINE DESULFURIZATION - CASE 2*

Refinery Capacity, BPCD	100,000	44,000	16,000
Investment for Desulfurization Facilities, Million Dollars	11.1	7.5	4.4
Years to Payout	5.0	5.0	5.0
Million Dollars Per Year:			
Cash flow	2.22	1.50	0.88
Depreciation	0.74	0.50	0.29
Net Profit	1.48	1.00	0.59
Income Tax	1.48	1.00	0.59
Gross Margin	2.96	2.00	1.18
Operating Costs:			
Depreciation	0.74	0.50	0.29
Operating Manpower	0.32	0.32	0.22
Utilities	2.09	0.92	0.33
Catalyst Replacement	0.23	0.10	0.04
Interest	0.56	0.38	0.22
Maintenance	0.36	0.26	0.16
Local Taxes and Insurance	0.15	0.11	0.06
Credit for Added Products	-1.00	-0.44	-0.16
Credit for Lower Butane Charges	-0.34	-0.15	-0.05
Total Operating Costs	<u>3.11</u>	<u>2.00</u>	<u>1.11</u>
Total Added Costs for Low-Sulfur Gasolines:			
Million Dollars Per Year (Gross Margin + Operating Costs)	6.07	4.00	2.29
Cents Per Gallon Gasoline	0.67	1.01	1.59

*Compared to Case 1

Table 2-7. INVESTMENT FOR DESULFURIZATION FACILITIES

	100,000 BPCD		44,000 BPCD		16,000 BPCD	
	Unit Capacity	Invest.* MM\$	Unit Capacity	Invest.* MM\$	Unit Capacity	Invest.* MM\$
Light Gasoline Hydrosulfurizer	4,700 BPSD	2.8	4,300 BPSD	2.0	1,600	1.3
Hydrosulfurizer for FCC Feedstock	35,000 BPSD	5.6	16,000 BPSD	3.6	6,000	2.1
Sulfur Recovery (Claus Plant)	15 Ton/Day	0.3	7 Ton/Day	0.2	None	-
Onsite Subtotal		8.7		5.8		3.4
Offsite		2.4		1.7		1.0
Total Investment		11.1		7.5		4.4

* Investment include paid-up royalty (if applicable) plus initial charge for catalyst.

Table 2-8. COMPARISON OF YIELDS - CASE 1 AND CASE 2

	BPCD		
	<u>Case 1</u>	<u>Case 2</u>	<u>Difference</u> (Case 2-Case 1)
<u>Charges</u>			
Crude Oil	100,000	100,000	-
Isobutane	863	1,103	240
N-Butane	3,964	3,599	-365
	<hr/>	<hr/>	<hr/>
Total Charges	104,827	104,702	-125
<u>Products</u>			
Fuel Gas, F.O.E.	4,060	3,908	-152
LPG (Propane-Propylene)	3,391	3,698	307
Gasolines	58,306	58,670	364
Kerosine	8,500	8,500	-
Diesel Fuel	8,200	8,200	-
No. 2 Furnace Oil	16,023	15,663	-360
No. 6 Fuel Oil	5,324	5,529	205
Delayed Coke (5 Bbl = 1 Ton)	1,008	1,008	-
Asphalt	3,100	3,100	-
Sulfur	(20 tons/day)	(34 tons/day)	(14 tons/day)
	<hr/>	<hr/>	<hr/>
Total Products (Excluding Sulfur)	107,912	108,276	364
Apparent Gain (Products Minus Charges)	3,085	3,574	489

Table 2-9. UTILITIES AND CATALYST REPLACEMENT - CASE 2*

<u>Process Unit</u>	<u>Light Gasoline Hydro- Desulfurization</u>	<u>FCC Feed Hydro- Desulfurization</u>	<u>Sulfur Recovery</u>	<u>Total</u>
Capacity	9,700 BPSD	36,000 BPSD	15 TPD	
Consumption of Utilities:				
Electricity, KW	240	1,800	30	2,070
Fuel, MM Btu/Hr	24	126	1	151
Cooling Water, GPM	400	1,260	3,940	5,600
Boiler Feedwater, lb/hr		1,100	4,000	5,100
Steam Consumed, lb/hr				
Steam Generated, lb/hr		1,100	3,800	4,900
Wash Water, GPM	10	40		50
Cost of Utilities, \$/CD				5,720
Catalyst Replacement, \$/CD	40	620		660
Fuel Equivalent of Utilities, BPCD (F.O.E.)				650

*Utilities and catalyst replacement are incremental above those in Case 1.

utilities and catalyst replacement cost in Case 2.

The apparent liquid gain in products over charges for Case 2 is 489 BPCD above Case 1. However, the utilities for the desulfurization facilities would require 650 BPCD of fuel equivalent. Thus, Case 2 would show a net loss of 161 BPCD in comparison to Case 1.

Investment to Produce Low-sulfur Gasolines in the
United States - Case 2

Based on the process scheme shown in Case 2, a crude oil throughput at 15 million barrels per day in 1978, and investment for the new desulfurization facilities at January, 1974 costs, the total investment would add about 2.03 billion dollars to U.S. refinery facilities. This investment would be portioned depending upon refinery size as follows:

<u>Range of Refinery Crude Capacity, BPSD</u>	<u>% of Crude Capacity</u>	<u>Investment, Million Dollars</u>
0 to 25,000	7.5	310
25,000 to 75,000	20.4	520
75,000 and larger	<u>72.1</u>	<u>1,200</u>
	100.0	2,030

This investment applies to the typical U.S. refineries and could be higher depending upon future imports of high sulfur crude oils. Increased imports of high sulfur crude oils would require desulfurization at increased severities for streams presently being desulfurized and installation of desulfurization facilities for other refinery streams.

In this event hydrogen for the refinery needs may not be sufficiently available from the reformer and new hydrogen production facilities may be required.

Potential Gasoline Production in Case 2 with Lead
Phase-Down

The potential production of no-lead, premium, and regular gasolines was calculated attempting to meet the EPA regulations on lead phase-down using the blending components produced in Case 2. All the gasolines would be low-sulfur. These results (Table 2-10) indicate that the projected percent of gasoline sales and EPA regulations on lead phase-down can be met through 1978. In 1979, octane upgrading would be required to meet the EPA regulations on lead content.

Table 2-10. POTENTIAL GASOLINE PRODUCTION IN CASE 2⁽¹⁾
WITH LEAD PHASE-DOWN

Year	1976	1977	1978	1979 ⁽²⁾
<u>Lead Content, g/gal</u>				
Allowed by EPA	1.4	1.0	0.8	0.5
Total Gasoline Pool	1.1	1.0	0.8	0.8
Premium Gasoline	1.8	1.8	1.8	1.8
Regular Gasoline	1.5	1.7	1.4	1.9
<u>Potential Gasoline, vol%</u>				
No-Lead (92 RON)	30	40	49	57
Premium (100 RON)	18	14	9	5
Regular (94 RON)	52	46	42	38
<u>No-Lead Gasoline, vol%</u>				
N-Butane	11	11	11	11
Alkylate	11	11	11	11
Reformate	33	33	33	33
FCC Gasoline	40	40	40	40
Light Gasoline	5	5	5	5
<u>From Cat Gasoline, vol%</u>				
N-Butane	12	12	12	12
Alkylate	36	36	36	36
Reformate	19	19	19	19
FCC Gasoline	33	33	33	33
Light Gasoline	--	--	--	--
<u>Regular Gasoline, vol%</u>				
N-Butane	10	10	10	10
Alkylate	--	1	3	4
Reformate	29	27	25	23
FCC Gasoline	32	30	28	26
Light Gasoline	29	30	31	34
POS Gasoline	2	2	3	3
<u>Gasoline Octane</u>				
No-Lead, Research	92.2	92.2	92.2	92.2
Motor	84.3	84.3	84.3	84.3
Premium, Research	100.2	100.2	100.2	100.2
Motor	95.6	95.6	96.5	96.5
Regular, Research	94.2	94.2	94.2	94.2
Motor	87.2	87.5	87.8	88.3

(1) Potential gasoline blends are based on the gasoline yields and properties from Case 2, "A" Typical U.S. Refinery with Hydrodesulfurization of Cat Cracker Feed, Light Virgin Gasoline and Light Coker Gasoline".

(2) In 1979, lead content of total gasoline pool would exceed EPA regulation.

CASE 3

"A" REFINERY WITH HYDRODESULFURIZATION OF CATALYTICALLY CRACKED AND LIGHT GASOLINES (CASE 3)

Case 3 considers the cost to produce low-sulfur gasolines by hydrodesulfurization of the catalytically cracked gasoline rather than the feedstock to the catalytic cracker.

The refinery process units in Case 3 would be the same as in Case 1 with the following additions:

- FCC Gasoline Hydrodesulfurization
- Light Gasoline Hydrodesulfurization

Figure 2-5 is a block flow diagram of Case 3 showing the yields and properties of the intermediate and final product streams. The yields and product properties are compared with those for the U.S. average and Cases 1 and 2 in Table 2-2.

Sulfur removal from the FCC gasoline of about 80 percent was selected since this yields about the same sulfur content in the total gasolines as in Case 2. At this desulfurization severity, 45 percent of the FCC gasoline would be hydrogenated, which would result in decreased research octane. The octane debit and other results are summarized as follows:

- Table 2-11 - Octane Debit
- Table 2-12 - Economics of Producing Low-Sulfur Gasoline

- Table 2-13 - Investment for Desulfurization Facilities
- Table 2-14 - Comparison of Yields, Case 1 versus and Case 3
- Table 2-15 - Utilities and Catalyst Replacement Requirements

The apparent gain (difference between products and charges, Table 2-14 for Case 3 would be 6 BPCD above the apparent gain for Case 1. However, the utilities for the desulfurization facilities would require 501 BPCD of equivalent fuel oil (Table XV). Thus Case 3 would result in a net loss of 495 BPCD compared to Case 1.

Economics as shown in Table 2-12 indicate that the total added costs (above Case 1) would be 0.82 cents per gallon to produce low sulfur gasolines. These costs include the penalty of 0.30 cents per gallon of gasoline debited to the lower octanes which result from partial hydrogenation of olefins in the FCC gasoline.

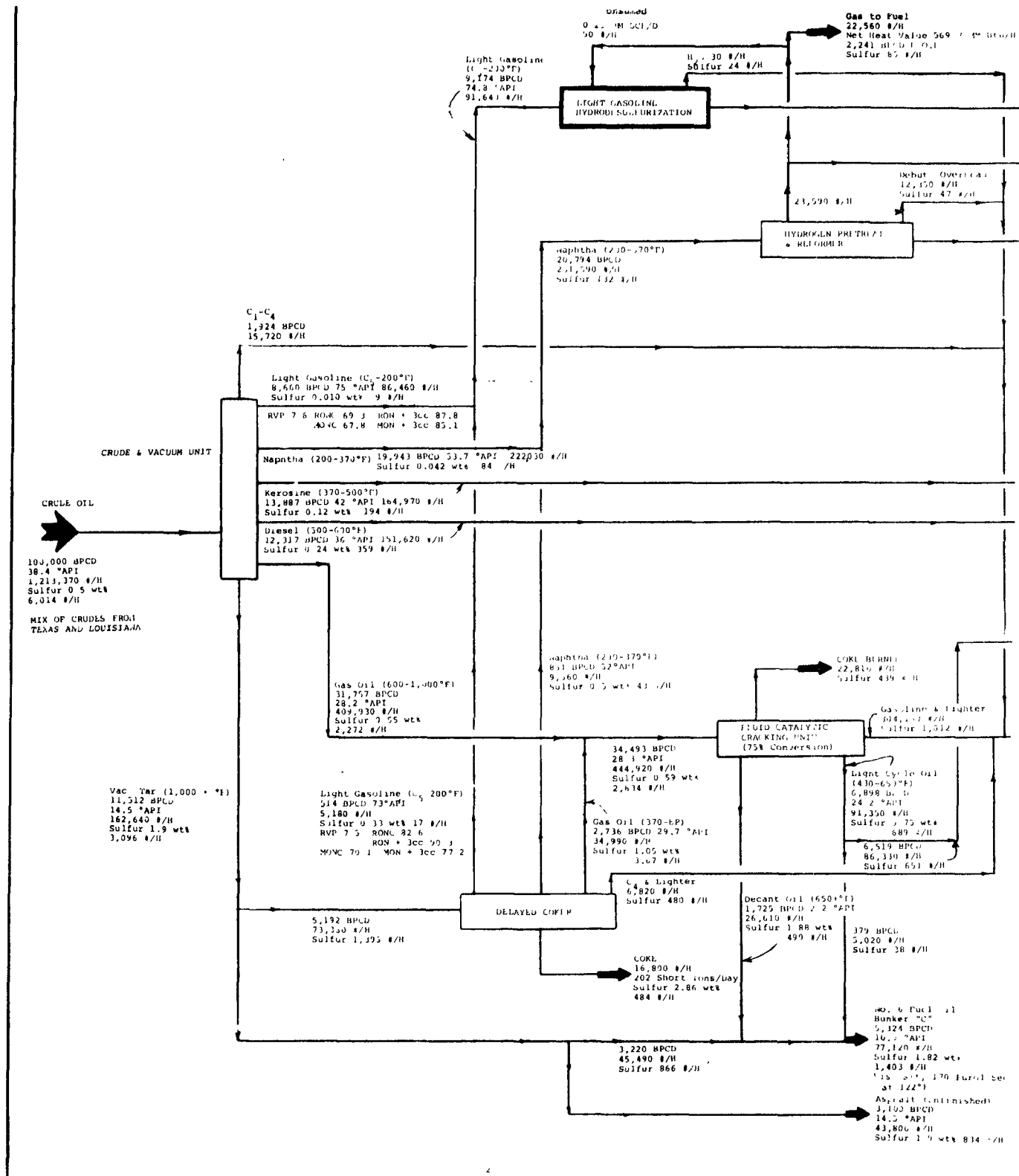


Figure 2-5. A typical U.S. refinery with hydrodesulfurization

Table 2-11. OCTANE DEBIT FOR CASE 3*

	<u>Octane at 0.5 g/gal</u>
<u>Case 1</u>	
Research	93.1
Motor	85.9
<u>Research + Motor</u> 2	89.5
 <u>Case 3</u>	
Research	92.2
Motor	85.9
<u>Research + Motor</u> 2	89.1

Research Octane Penalty = 93.1 - 92.2 = 0.9 Octane

$$\begin{aligned}
 \text{Octane Debit} &= \frac{0.9 \text{ Octane}}{6 \text{ Octane, Gal}} \times \frac{\$0.02}{\text{Day}} \times \frac{58,520 \text{ Bbls}}{\text{Day}} \times \frac{42 \text{ Gal}}{\text{Bbl}} \times \frac{365 \text{ Days}}{\text{Year}} \\
 &= \$2.69 \text{ million/year} \\
 &\text{or } 0.30 \text{ cents per gallon of gasoline.}
 \end{aligned}$$

*Compared to Case 1

Table 2-12. COST FOR GASOLINE DESULFURIZATION - CASE 3*

Refinery Capacity	100,000 BPCD
Investment for Desulfurization Facilities	\$8.3 million
Years to Payout	5
Million Dollars Per Year:	
Cash Flow	1.66
Depreciation	0.55
Net Profit	1.11
Income Tax	1.11
Gross Margin	2.22
Operating Costs:	
Depreciation	0.55
Operating Manpower	0.22
Utilities	0.91
Catalyst Replacement	0.04
Interest	0.42
Maintenance	0.29
Local Taxes and Insurance	0.01
Credit for Added Products	-0.06
Cost for Added Butane	0.04
Debit for Lower Octane	2.69
Total Operating Costs	<u>5.11</u>
Total Added Cost for Low-Sulfur Gasolines (Gross Margin + Operating Costs)	7.33
Cents Per Gallon Gasoline	0.82

Table 2-13. INVESTMENT FOR DESULFURIZATION FACILITIES - CASE 3

	<u>Capacity</u>	<u>Investment *</u> <u>Million Dollars</u>
Refinery	100,000 BPCD	-----
Light Gasoline Hydrodesulfurizer Unit	9,700 BPSD	2.8
FCC Gasoline Hydrodesulfurizer Unit	21,600 BPSD	<u>3.6</u>
Onsite Subtotal		6.4
Offsite		<u><u>1.9</u></u>
Total Investment		8.3

Table 2-14. COMPARISON OF YIELDS - CASE 1 AND CASE 3

	BPCD		
	<u>Case 1</u>	<u>Case 3</u>	<u>Difference</u> (Case 3-Case 1)
<u>Charges</u>			
Crude Oil	100,000	100,000	----
Isobutane	863	863	----
N-Butane	<u>3,964</u>	<u>3,979</u>	<u>15</u>
Total Charges	104,827	104,842	15
<u>Products</u>			
Fuel Gas, F.O.E.	4,060	3,867	-193
LPG (Propane-Propylene)	3,391	3,391	----
Gasolines	58,306	58,520	214
Kerosine	8,500	8,500	----
Diesel Fuel	8,200	8,200	----
No. 2 Furnace Oil	16,023	16,023	----
No. 6 Fuel Oil	5,324	5,324	----
Delayed Coke (5 Bbl = 1 Ton)	1,008	1,008	----
Asphalt	3,100	3,100	----
Sulfur	<u>(20 ton/day)</u>	<u>(22 ton/day)</u>	<u>(2 ton/day)</u>
Total Products (Excluding Sulfur)	107,912	107,933	21
Apparent Gain (Products Minus Charges)	3,085	3,091	6

Table 2-15. UTILITIES AND CATALYST REPLACEMENT - CASE 3*

<u>Process Unit</u>	<u>Light Gasoline Hydro- Desulfurization</u>	<u>Light Gasoline Hydro- Desulfurization</u>	<u>Total</u>
Capacity	9,700 BPSD	21,600 BPSD	
Consumption of Utilities:			
Electricity, KW	240	1,070	1,310
Fuel, MM Btu/H	24	90	114
Cooling Water, GPM	400	1,430	1,830
Wash Water, GPM	10	30	40
Cost of Utilities, \$/CD			2,490
Catalyst Replacement, \$CD	40	70	110
Fuel Equivalent of Utilities, BPCD (F.O.E.)			501

*Utilities and catalyst replacement are incremental above those in Case 1.

SULFUR DISTRIBUTION

The sulfur contained in the crude oil to the refinery is distributed in the products, recovered as elemental sulfur, and emitted as SO_2 to atmosphere as shown in Table 2-16 for all three cases studied.

Sulfur contained in the gasoline is only a small fraction of the sulfur in the crude oil. Sulfur in the products used as fuels eventually will be emitted as sulfur oxides to the atmosphere as products of combustion unless stack gas scrubbing or other types of controls are used. The sulfur in delayed coke may be emitted as sulfur oxides to the atmosphere or be combined in metallurgical slag, depending upon the use of the delayed coke.

From the values tabulated in Table 2-16, it is seen that hydrosulfurization of the gas oil feedstock to catalytic cracking (Case 2) results in:

- gasoline with the same sulfur content as Case 3 but lower than Case 1
- diesel fuel, No. 2 furnace oil and Banker "C" with lower sulfur than either Case 1 or 3
- increased recovery of elemental sulfur

Table 2-16. SULFUR DISTRIBUTION

<u>Sulfur Content, Lb/hr</u>	<u>Case 1</u>	<u>Case 2</u>	<u>Case 3</u>
Crude Oil	6,014	6,014	6,014
Products:			
Gasoline	191	38	38
Kerosine	119	119	119
Diesel Fuel	148	135	148
No. 2 Furnace Oil	554	271	554
Bunker C	1,403	987	1,403
Asphalt	834	834	834
Delayed Coke	484	484	484
Recovered as Elemental Sulfur	1,669	2,834	1,814
Emitted as SO ₂ to Atmosphere	612	312	620
Total	6,014	6,014	6,014
<u>Sulfur Distribution, %*</u>			
Gasoline	3.2	0.6	0.6
Kerosine	2.0	2.0	2.0
Diesel Fuel	2.5	2.2	2.5
No.2 Furnace Oil	9.2	4.5	9.2
Bunker C	23.3	16.4	23.3
Asphalt	13.9	13.9	13.9
Delayed Coke	8.0	8.0	8.0
Recovered as Elemental Sulfur	27.7	47.2	30.2
Emitted as SO ₂ to Atmosphere	10.2	5.2	10.3
Total	100.0	100.0	100.0

*As percent of sulfur in crude oil

APPENDIX A
GENERAL SITUATIONS OF REFINERIES IN THE UNITED STATES

No two crude oils or two refineries are the same. Furthermore, no two refineries will produce and have the same product demand. Depending upon the crude properties and refinery process capabilities, different refineries are geared to the following categories or combinations thereof:

- Production of gasolines, mid-distillates and residual oil
- Petrochemical production
- Lubricant production
- Asphalt production

United States refineries produce petroleum products in relation to the market demands for quantities and properties. Each refinery bases its operations on market demands and availability of crudes within the limitations of its refinery process units and the flexibility of operating conditions.

In crude topping and vacuum operations, crude oils can be distilled into fractions with true boiling cut points approximately as follows:

- Butanes and lighter components to gas recovery
- Pentanes to 200°F light gasoline for blending to gasoline or isomerization of the pentanes and hexanes to upgrade the octane number
- 200°F - 370°F naphtha for reformer feedstock to upgrade the octane number or produce aromatics

- 600°F - 1,000°F gas oil feedstock to catalytic cracking, thermal cracking or hydrocracking
- Heavier than 1,000°F residuum for blending No. 6 fuel oil or to asphalt or produced as feedstock for visbreaking, delayed coking, fluid coking or solvent deasphalting

Typical ASTM distillations of refined products to sales are shown in Figure A-1. Gasolines distill in the range of 80°F to 400°F, kerosine and jet fuel (kerosine-type) distill in the range of 340°F to 530°F and diesel fuel and No. 2 fuel oil distill in the range of 350°F to 650°F. The term "mid-distillates" refers to the distillates boiling between gasoline and No. 6 fuel oil and comprises the kerosine, aviation jet fuel, diesel fuels and No. 2 heating oil. Kerosine, aviation jet fuel and No. 1-D diesel fuel are produced from the distillates boiling between 370°F and 500°F true boiling cut points. No. 2 heating oil and No. 2-D diesel fuel are blends of essentially 50 percent of the 370°F to 500°F fraction with 50 percent of the 500°F to 600°F fraction.

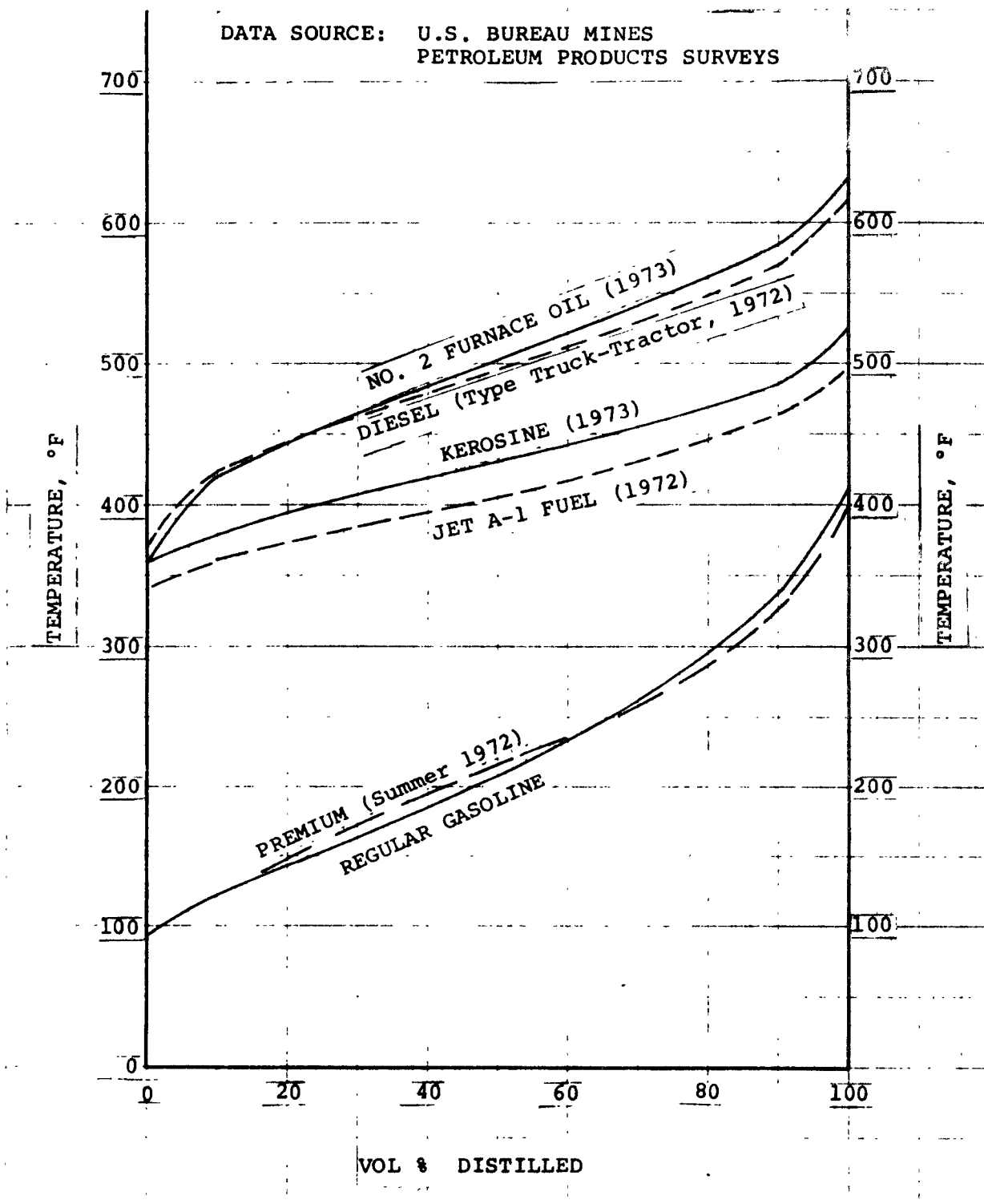


Figure A-1. Typical ASTM Distillations
of Petroleum Products.

APPENDIX B
U.S. PRODUCTION OF PETROLEUM PRODUCTS

Table B-1 shows the range of crude capacities in U. S. refineries in 1973. Refineries larger than 25,000 BPSD have 92.5% of the U.S. crude capacity. The median quantity of crude is processed in U.S. refineries of about 100,000 BPSD crude capacity.

Table B-2 shows the charge capacity of U. S. refineries in 1973 by types of processing units.

Table B-3 shows the production U. S. refinery products in 1971. Table B-4 shows the U. S. demand for mid-distillates by use in 1973.

Table B-5 shows typical properties of the petroleum products sold in the United States in 1972 and 1973.

The 1972 properties of the total U.S. gasoline pool were estimated from U.S. Bureau of Mines surveys and Ethyl Corporation sales data as follows:

Research Octane	97.5
Motor Octane	90.0
Lead, g/gal.	2.24
Sulfur, wt%	0.031

The response of lead content in the total U.S. gasoline pool was estimated from the lead response of various premium and regular gasoline blends. Figure B-1 shows the research and motor octanes of the total U.S. gasoline pool in 1972 as a function of lead content.

Table B-1. CRUDE CAPACITIES OF U.S. REFINERIES IN 1973

<u>Range of Crude Capacities, BPSD</u>	<u>Number of Refineries</u>	<u>Crude Capacity, BPSD</u>		<u>% of U.S. Crude Capacity</u>
		<u>Total</u>	<u>Average</u>	
0-10,000	76	340,000	4,500	2.4
10,000-25,000	43	702,000	16,000	5.1
25,000-75,000	64	2,826,000	44,000	20.4
75,000-125,000	31	3,033,000	98,000	21.9
125,000-200,000	15	2,298,000	153,000	16.5
200,000-300,000	8	2,145,000	268,000	15.4
Larger Than 300,000	<u>7</u>	<u>2,546,000</u>	364,000	<u>18.3</u>
Total	244	13,890,000		100.0
Refineries Larger Than 25,000 BPSD	125	12,848,000	103,000	92.5

Table B-2. CAPACITY OF PROCESS UNITS IN UNITED STATES IN 1973

<u>Process Unit</u>	<u>Charge Capacity, BPSD</u>	<u>Vol. % of Crude Capacity</u>	
Crude Distillation	13,890,000	100.0	
Vacuum Distillation	5,150,700	36.8	
Delayed Cokers	776,900	5.6	} 6.4
Fluid Cokers	118,200	0.8	
Visbreakers	237,300	1.7	
Hydrogen Desulfurization:			
Naphtha	2,798,800	20.0	
Mid-Distillates	1,109,700	7.9	
FCC Feedstock	279,800	2.0	
Heavy Gas Oil	184,000	1.3	
Reduced Crude	19,500	0.14	
Cat Crackers (Fresh Feed)	4,512,600	32.3	
Hydrocrackers	865,100	6.2	
Cat Reformers	3,278,100	23.4	
Alkylation (Sulfuric Acid)	531,300	3.8	} 5.8
Alkylation (Hydrofluoric Acid)	280,600	2.0	
Aromatics (Benzene-Toluene-Xylenes)	188,500	1.3	
Isomerization			
Butane	49,600	0.35	
Pentane	34,100	0.24	
Pentane-Hexane	37,500	0.27	
Lubes	221,900	1.6	
Asphalt	644,300	4.6	
Coke	(42,700 ton/day)	(0.00305 tons coke per barrel crude)	

Table B-3. U. S. REFINERY PRODUCTS IN 1971

<u>Refinery Input</u>	<u>Million Barrels</u>	<u>Input, %*</u>
Crude Runs to Still	4,088	100.0
Natural Gas Liquids	359	8.8
	<u>4,447</u>	<u>108.8</u>
<u>Refinery Production</u>	<u>Million Barrels</u>	<u>Yield, %*</u>
Motor Gasoline	2,179	53.3
Aviation Gasoline	18	0.4
Naphtha in Naphtha-Type Jet Fuel	43	1.1
Special Naphthas	28	0.7
Petrochemical Feedstocks	111	2.7
Total Gasoline-Naphtha	<u>2,379</u>	<u>58.2</u>
Ethane-Ethylene	9	0.2
Liquefied Petroleum Gas (LPG)	32	0.8
Propane-Propylene	12	0.3
C ₃ -C ₄ Mix	3	0.1
Total Light Components	<u>56</u>	<u>1.4</u>
Kerosine	87	2.1
Kerosine-Type Jet Fuel	219	5.4
Kerosine in Naphtha-Type Jet Fuel	42	1.0
Total Kerosine	<u>348</u>	<u>8.5</u>
Distillate Fuel Oil	911	22.3
Residual Fuel Oil	275	6.7
Asphalt (5.5 bbl = 1 short ton)	157	3.8
Road Oil	9	0.2
Total Residual Oil	<u>441</u>	<u>10.8</u>
Lubricants	65	1.6
Wax (1 bbl = 280 lb)	7	0.2
	<u>72</u>	<u>1.8</u>
Coke (5 bbl = 1 short ton)	62	1.5
Miscellaneous Products	14	0.3
Still Gas to Fuel	157	3.8
C ₃ to Fuel	5	0.1
C ₄ to Fuel	14	0.3
LPG to Fuel	3	0.1
	<u>179</u>	<u>4.3</u>
Accounted Yield	<u>4,462</u>	<u>109.1</u>
Difference (Accounted Minus Input)	15	0.3

*Volume percent on crude input

Table B-4. U.S. DEMAND FOR MID-DISTILLATES BY USE IN 1973

	Million Barrels	%
Kerosine	80	6.1
Kerosine-type Jet Fuel	233	17.6
Kerosine Content of Naphtha-type Jet Fuel	38	2.9
No. 1 Range Oil	15	1.1
	<u>366</u>	<u>27.7</u>
Diesel Fuel Used on Highways	164	12.4
Industrial Uses	50	3.8
Oil Company Fuel	14	1.1
Railroads	86	6.5
Vessel Bunkering	21	1.6
Military Uses	17	1.3
	<u>352</u>	<u>26.7</u>
Heating Oil	509	38.5
Gas and Electric Company Public Utility Power Plants	35	2.6
	<u>544</u>	<u>41.1</u>
Miscellaneous and Unaccounted	60	4.5
Total Mid-distillates	<u>1,322</u>	<u>100.0</u>

Table B-5. TYPICAL PROPERTIES OF PETROLEUM PRODUCTS

	REGULAR GASOLINE	PREMIUM GASOLINE	REGULAR GASOLINE	PREMIUM GASOLINE	TOTAL GASOLINE POOL	KEROSENE	JET A-1 FUEL	DIESEL FUEL (TRUCKS, TRACTORS)	NO. 2 FURNACE OIL	NO. 6
U.S. Bureau Mines Survey	Summer 1972	Summer 1972	Winter 1972-73	Winter 1972-73	Average 1972	1973	1972	1972	1973	1973
Gravity, °API	60.5	60.7	62.5	63.0	61.7	42.3	42.4	36.5	35.1	11.0
Distillation, ASTM, °F										
IBP	92	91	84	84		341	362	375	367	
10%	122	123	108	109		378		427	425	
30	163	172	150	158						
50	208	217	200	209		428	405	495	504	
70	262	257	257	251		485	464	573	589	
90%	339	324	334	352		525		618	635	
EP	411	401	405	397						
Sulfur, wt %	0.042	0.026	0.038	0.023		0.067	0.065	0.21	0.22	1.60
Aniline Point, °F						146	140	147	144	
Cetane Number								48.6		
Viscosity, CS at 100°F						1.66		2.71	2.71	170
Viscosity, Furol at 122°F										0.3
Carbon Residue, wt %										
Lead, g/gal.										
Octane Number										
Research	2.04	2.52	1.80	2.34						
Motor	94.1	99.8	93.9	99.6						
(Research + Motor)/2	86.4	92.2	86.4	92.2						
Reid Vapor Pressure	33	96.0	90.2	93.9						
	9.2	9.3	12.2	12.1						
Total Gasoline:										
Sales, %	38	62	37	63	0.031					
Sulfur, wt %	0.032		0.029		97.5					
Research Octane	97.6		97.5		90.0					
Motor Octane	90.0		90.1		93.8					
(Research + Motor)/2	93.8		93.8		2.24					
Lead, g/gal.	2.34		2.14		10.7					
Reid Vapor Pressure										

LEAD ALKYL ANTIKNOCK SUSCEPTIBILITY CHART

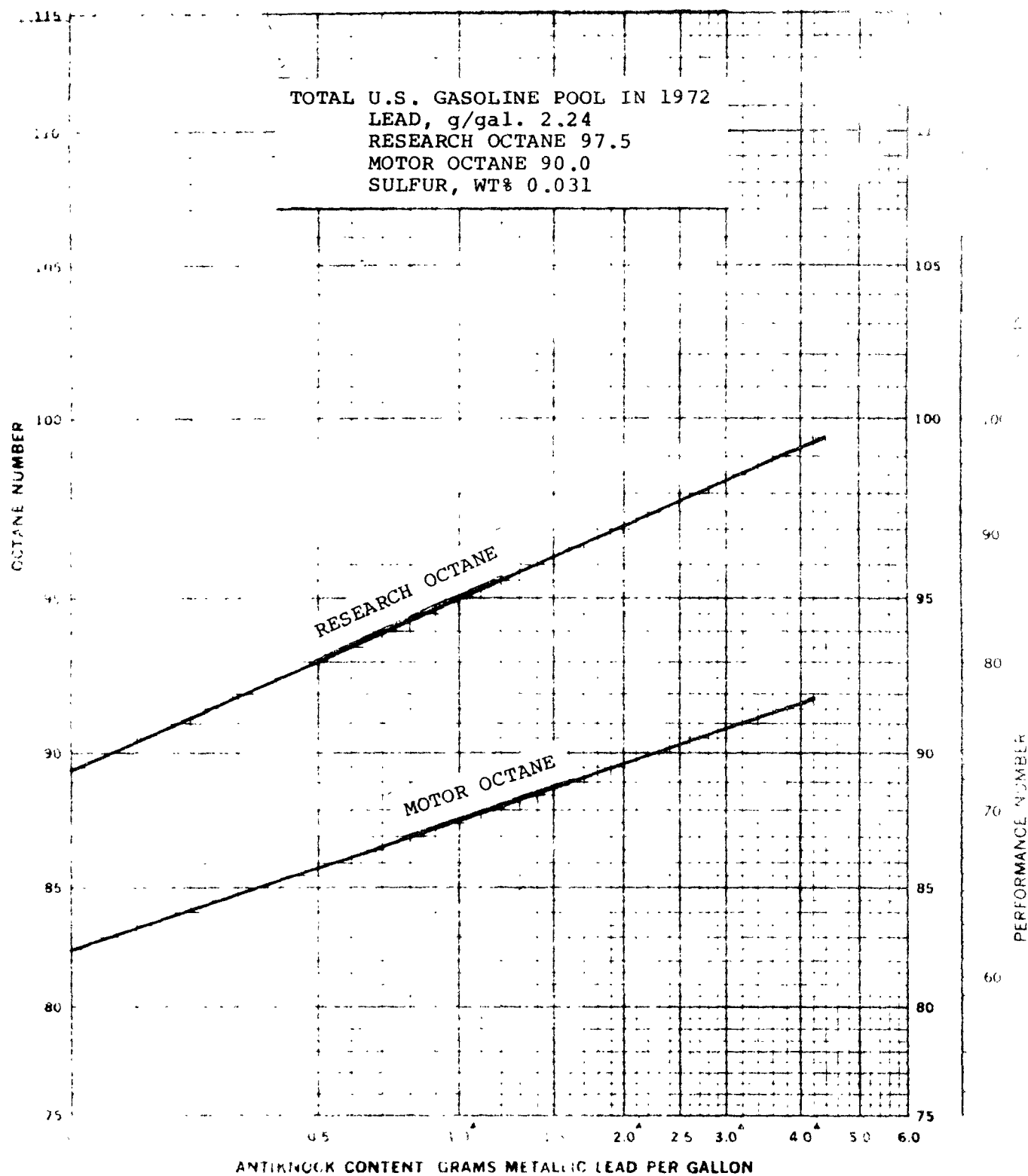


Figure B-1. Octane of Total U. S. Gasoline Pool in 1972.

APPENDIX C
COSTS

1. All costs and capital are based on January, 1974 levels.
2. Capital related charges
 - Straight-line depreciation for 15 year life
 - Interest at 10 percent per year. This is equivalent to 5 percent per year over the average payout period.
 - Maintenance: onsite, 4 percent; offsite, 2 percent
 - Local taxes and insurance: 1.5 percent
 - Payout on investment: 5 years after taxes
3. U.S. income plus state corporation taxes at 50 percent of gross profit.
4. Incremental utility costs for new facilities
 - Fuel: \$1.40 per million Btu net heat value. This is equivalent to \$7.50 per barrel of 38°API crude oil.
 - Electricity:

	<u>\$ Per KWH</u>
Fuel cost	0.014
Other charges	<u>0.006</u>
	0.020
 - Steam:
 - \$1.90 per 1,000 pounds corresponding to the fuel cost of \$1.40 per million Btu.
 - Cooling Water:
 - \$0.20 per 1,000 gallons circulation
 - Treated boiler feedwater:
 - \$0.05 per 1,000 pounds
5. Operating manpower costs
 - Average costs for stillman and operators at \$6.00 per hour plus 30 percent fringe benefits. Sixty percent overhead on operating manpower is added to allow for supervision, laboratory, technical service

and instrument services.

<u>Manpower Cost</u> <u>Per Shift Position</u>	<u>\$/HR</u>	<u>%</u>	<u>\$/YR</u>
Rate	6.00		52,600
Fringe Benefits		30	15,800
Overhead		60	<u>41,000</u>
TOTAL			109,400

6. Product prices

Incremental product yields were priced at the same price as crude oil (\$7.50 per barrel).

7. Royalties

Gas oil hydrodesulfurization:

Paid-up royalty \$10.00 per BPCD feed rate

Naphtha hydrodesulfurization:

Royalty-free. Royalty costs would be included in catalyst costs or nominal know-how fee.

8. Hydrogen make-up

Assumed to be available in the reformer make-gas for hydrodesulfurization units.

9. Gasoline octane

Incremental gasoline octane priced at 2.0 cents per 6 octane difference between premium and regular gasolines at the 1972 lead level of 2.24 grams per gallon. This price is equivalent to 0.333 cents per gallon per research octane number.

APPENDIX D
OIL EQUIVALENT OF UTILITIES

1. Fuel

Net heat value at 6.1 million Btu per barrel fuel oil equivalent. (F.O.E.)

2. Electricity

Net heat to generate electricity is assumed to be 10,000 Btu per kilowatt-hour. This requires 0.04 BPCD F.O.E. per kilowatt-hour.

3. Steam

Net heat to generate steam is assumed to be 1,370 Btu per pound of steam. This requires 5.4 BPCD F.O.E. per 1,000 pounds per hour of steam.

APPENDIX E
SOURCES OF INFORMATION

American Petroleum Institute

"Annual Statistical Review, U.S. Petroleum
Industry Statistics, 1972"

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Directory"

CHAPTER 1

INTRODUCTION

This part of the report covers work which was performed under Contract 68-02-1308 for the Environmental Protection Agency (EPA), Office of Research and Monitoring, Task 10, Phase 3.

The purpose of this work is to determine the impact of producing low-sulfur gasolines on the refineries supplying California and the Los Angeles area. Refineries in the Los Angeles area account for 56% of the crude capacity in California. For this work, the basic refinery was considered to have process units with capacities based on percent of crude input to be the average of refineries within California charging a crude mix with the average composition of crudes now being processed in California. Desulfurization facilities were then added to this basic refinery, using two processing schemes, to produce low-sulfur gasolines.

Refineries in California process crude mixes averaging 53% domestic crudes and 47% foreign crudes. The California crude oils are heavy crudes with high sulfur content. As the results of the heavy high sulfur charge stocks and the market demands in California, these refineries have more residual oil processing, more hydrogen treating of products, and more hydrocracking of gas oils than the "typical" refineries in the United States.

In order to show the maximum costs for producing low-sulfur gasolines, it was assumed that new facilities would be necessary to provide the incremental hydrogen, remove hydrogen sulfide and recover sulfur.

Part 2 of this report (Phase 2) presented a similar study based on a "typical" U. S. refinery and crude oil mix. The Phase 3 work supplements the Phase 2 report.

CHAPTER 2

SUMMARY

This study shows how a model of the average refineries in California can produce no-lead, low-sulfur gasoline and by installing new hydrodesulfurization facilities can produce low-sulfur gasolines to include the no-lead, premium, and regular gasolines.

Results of this study show that the existing large California refineries can produce no-lead, low-sulfur gasoline at the projected percent of gasolines sales through 1979, blended from normal butane, light hydrocrackate, reformate, and alkylate. Beyond 1976, the predicted demand of no-lead and premium gasolines could not be met with EPA limits on lead anti-knock in the total gasoline pool.

Total gasolines can be made low-sulfur by hydrodesulfurization of the gas oil feedstock to catalytic cracking and by hydrodesulfurization of the light virgin gasoline and light thermally cracked gasolines. Economics for this scheme (Case 2) show that the costs** for producing low-sulfur gasoline would add 1.1 cents per gallon to the costs of manufacturing the present gasolines in refineries of 100,000 barrels per calendar day (bpcd) capacities.

An alternate case considers hydrodesulfurization of the catalytically cracked gasoline rather than the feedstock to the catalytic cracker. Economics indicate that this scheme (Case 3) to produce low-sulfur gasoline would add about 1.0 cent per gallon to the present cost** of manufacturing gasolines in refineries of 100,000 bpcd capacities.

In California, there are eleven refineries which are larger than 75,000 bpsd.* The crude capacities for these eleven refineries total 1,402,000 bpsd which is 78% of the total crude capacity of all refineries in California. If new facilities were installed to produce low sulfur gasolines in these eleven refineries by desulfurizing the light virgin gasoline, light thermal gasolines, and catalytic cracker feedstock (Case 2), an investment of about 250 million dollars would be required based on May, 1974 costs.

Based on the gasoline yields and properties in Case 2 for low-sulfur gasolines, the predicted sales ratios of no-lead, premium, and regular gasolines could be blended and meet the EPA regulations on lead phase-down for 1975 and 1976. Additional processing for octane up-grading would be required starting in 1977 to meet the EPA regulations on further lead phase-down.

* bpsd - Barrels per stream day

bpcd - Barrels per calendar day

**Costs include 5 years payout on investment (20% rate of return) after taxes.

CHAPTER 3

PRODUCTION OF NO-LEAD, LOW-SULFUR GASOLINE IN PRESENT CALIFORNIA REFINERIES

CRUDE OILS RUN IN CALIFORNIA REFINERIES

At present, California refineries process about 53% domestic crudes and 47% imported crudes. Table 3-1 shows the origins of crudes processed in District 5 which includes California. The California crude oils are typically heavy and high sulfur crudes. The Middle East are also typically high sulfur crudes. Therefore, the average mixture of crudes processed in California refineries is heavier and has higher sulfur content than the crudes processed in the average U.S. refinery.

Table 3-2 lists the crude mix selected for this study. This crude mix would be 28°API, 1.27 wt% sulfur, and 4.1 wt% Conradson carbon.

When the Alyeska pipeline begins delivering North Slope crude oil in 1977, this crude will probably be processed by the West Coast refineries and reduce their imports of foreign crude oils.

Addition of Alaskan North Slope crude oil to the West Coast crude mix will not materially effect the crude mix as the North Slope crude is 26°API, 1.1 wt% sulfur, and 6.0 wt% Conradson carbon.

AVERAGE OF CALIFORNIA REFINERIES - CASE 1

As the results of processing heavy crude oils with high sulfur contents and sales demands, the California refineries have more residual oil processing, more hydrogen treating of products, and more hydrocracking of gas oils than the "typical" refineries in the United States.

Table 3-3 shows the capacities of processing units in California refineries.

The refinery process units selected for Case 1 for an "Average of California Refineries" were as follows:

- Crude and Vacuum Distillation
- Catalytic Reformer with Hydrogen Pretreat Section
- Fluid Catalytic Cracker with Vapor Recovery
- Catalytic Hydrocracker
- Jet Fuel Hydrotreater
- Diesel Hydrotreater
- Alkylation
- Delayed Coker
- Visbreaker
- Solvent Deasphalting
- Amine Treating and Sulfur Recovery

Table 3-1. CRUDE OILS FOR DISTRICT 5

	THOUSAND BARRELS PER DAY	VOL% OF TOTAL
Domestic Crudes:		
California	910	42.2
Alaska	190	8.8
Four-corners Pipeline	30	1.4
Rail From Utah	15	0.7
	<u>1,145</u>	<u>53.1</u>
Foreign Crudes:		
Canada	250	11.6
Venezuela	20	0.9
Ecuador, Peru	70	3.2
Middle East	470	21.9
Indonesia	200	9.3
	<u>1,010</u>	<u>46.9</u>
Total Crude Oils	<u><u>2,155</u></u>	<u><u>100.0</u></u>

From: Oil & Gas Journal, March 18, 1974

Table 3-2. SELECTED CRUDE MIX

	THOUSAND BARRELS PER DAY	VOL % OF TOTAL
California:	910	
Midway-Sunset		13
Huntington Beach		7
Wilmington		25
Alaska	190	9
Canada	250	13
Middle East (Arabian)	470	23
Indonesia (Minas)	<u>200</u>	<u>10</u>
Total	2,020	100

Table 3-3. PROCESSING UNITS IN CALIFORNIA REFINERIES

PROCESS UNIT	FEED CAPACITY BPSD		FEED CAPACITY VOL % ON CRUDE CAPACITY	
	Los Angeles Area	Total California	Los Angeles Area	Total California
Crude Distillation	996,000	1,785,200	100.0	100.0
Vacuum	509,500	930,000	51.2	52.1
Catalytic Cracking	284,500	473,500	28.6	26.5
Catalytic Hydrocracking	134,200	312,100	13.5	17.5
Thermal Cracking Gas Oil	23,000	32,500	2.3	1.8
Catalytic Reforming	245,700	463,700	24.7	26.0
Hydrotreating:				
Naphtha	234,000	425,400	23.5	23.8
Mid-Distillate	149,000	202,800	15.0	11.4
Other	-	64,000	-	3.6
Delayed Coking	210,000	252,500	21.1	14.1
Fluid Coking	-	71,000	-	4.0
Visbreaking	86,000	95,600	8.7	5.4
Alkylation, HF	15,800	15,800	1.6	0.9
Sulfuric Acid	33,600	73,000	3.4	4.1
Aromatics, BTX	4,000	5,500	0.4	0.3
Isomerization, C ₄	5,000	9,700	0.5	0.5
C ₅ & C ₆	13,000	13,000	1.3	0.7
Lubes	-	23,800	-	1.3
Asphalt	47,100	96,400	4.7	5.4
Solvent Deasphalting	-	45,000	-	2.5

Figure 3-1 shows the flow scheme for this "Average of California Refineries".

To calculate the refinery yields, the following conditions were assumed:

- Crude input to basic California refinery (Case 1) would be 100,000 bpcd crude oil.
- Catalytic cracker would operate at 75% conversion with yields corresponding to riser cracker with zeolite catalysts.
- Production of alkylate was set at 5.0 vol% on crude input by taking propylene to LPG.
- Reformer severity would produce 95 research octane clear.
- Unfinished asphalt would be produced from vacuum residuum and asphalt from solvent deasphalting.
- Production of lubricants and waxes were not considered as these account for only 0.9 vol% on crude input.
- Special naphthas and the benzene - toluene - xylenes aromatics were considered to be part of reformate and would be accounted in the total gasolines.

Capacities of the process units required to process the streams from the selected crude mix in Case 1 are compared in Table 3-4 with the average of California refineries based on percent of crude input.

Product yields and properties in Case 1 are compared in Table 3-5 with products produced in California refineries.

The comparisons in Table 3-4 and Table 3-5 show that refinery model and crude mix used in Case 1 may be considered an average of the California refineries.

For Case 1, the overall material balance is shown in Table 3-6 and the gasoline pool is shown in Table 3-7.

The volumetric blended octanes shown in Table 3-7 were corrected for sensitivities, olefin content and aromatic content. The corrected octanes are shown in Figure 3-2.

SALES OF PREMIUM AND NO-LEAD GASOLINES IN CALIFORNIA

During the period 1953 to 1972, the premium gasoline sales as percent of total gasoline sales in California has been 16 to 20% higher than the average for the United States.

Figure 3-3 shows a projected percent of sales of premium gasoline and no-lead gasoline in California. It was assumed that the premium gasoline would be 25% of sales in 1977. The sales requirements for premium gasoline will continue to decrease as the pre-1971 high

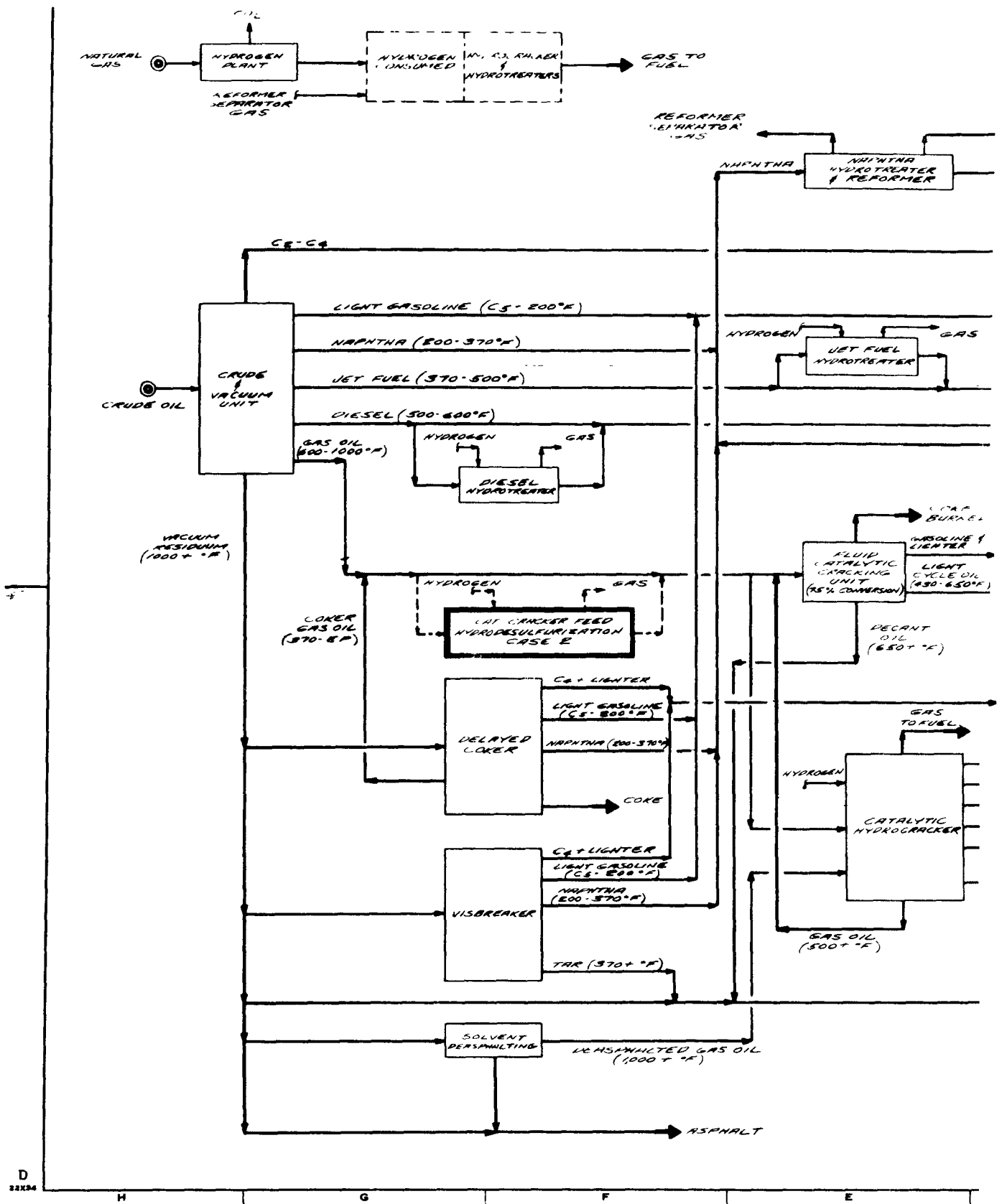


Figure 3-1. Flow schemes for

Table 3-4. CAPACITIES OF PROCESS UNITS IN CASE 1
COMPARED WITH CALIFORNIA REFINERIES

<u>PROCESS UNITS</u>	<u>VOL% OF CRUDE CAPACITY</u>	
	<u>Average of California Refineries in 1973</u>	<u>Case 1</u>
Crude Distillation	100.0	100.0
Vacuum Distillation	52.1	51.5*
Catalytic Cracking	26.5	24.4
Catalytic Hydrocracking	17.5	17.1
Thermal Cracking Gas Oil	1.8	-
Catalytic Reforming	26.0	24.0
Hydrotreating:		
Naphtha	23.8	15.8
Mid-Distillate	11.4	11.4
Other	3.6	-
Delayed Coking	14.1	12.3
Fluid Coking	4.0	-
Visbreaking	5.4	3.7
Alkylation, HF	0.9	5.0
Sulfuric Acid	4.1	
Aromatics, BTX Production	0.3	-
Isomerization, C ₄	0.5	-
C ₅ & C ₆	0.7	-
Lube Production	1.3	-
Asphalt Production	5.4	2.2
Solvent Deasphalting	2.5	1.7

*At 670° F TBP cut point in crude oil

Table 3-5. COMPARISON OF PRODUCTS AND YIELDS

Basis: Yields are Vol% on crude input and for West Coast (PA) District 5) for January 1972-September, 1973. Properties of products are from 1973 sales in California.

	<u>West Coast Production</u>	<u>Case 1</u>	<u>Case 2</u>	<u>Case 3</u>
<u>TOTAL GASOLINES</u>				
Yield, Vol % on Crude Input	51.0	55.5	55.5	55.5
°API	58.5	61.5	62.6	61.6
Sulfur, wt%	0.046	0.053	0.006	0.006
Lead Anti-knock, Grams Per Gal.	2.1	2.1	2.1	2.1
Research Octane	97.2	97.1	97.4	96.0
Motor Octane	89.0	89.6	90.4	90.8
Reid Vapor Pressure	10.0	10.0	10.0	10.0
<u>JET FUEL AND KEROSENE</u>				
Yield, Vol% on Crude Input	11.0	11.6	11.6	11.6
°API	42.9	39.0	39.0	39.0
Sulfur, wt%	0.045	0.049	0.049	0.049
Aniline Point, °F	143	139	139	139
<u>DIESEL AND NO. 2 FURNACE OIL</u>				
Yield, Vol% on Crude Input	13.7	14.8	14.8	14.8
°API	35.0	35.7	35.6	35.7
Sulfur, wt%	0.27	0.26	0.26	0.26
Cetane Index	50.0	48.8	48.8	48.8
<u>NO. 6 FUEL OIL</u>				
Yield, Vol% on Crude Input	17.4	14.6	14.6	14.6
°API	11.0	10.8	11.3	10.8
Sulfur, wt%	1.5	2.4	1.7	2.4
Carbon Residue, wt%	11.2	9.1	9.1	9.1
<u>OTHER PRODUCTS</u>				
Yield, Vol% on Crude Input:				
Coke (5 bbl = 1 Short Ton)	4.5	3.1	3.1	3.1
Asphalt and Road Oil	3.3	2.2	2.2	2.2
Still Gas to Fuel	4.7	3.8	3.7	3.8
Liquefied Refinery Gas	2.5	2.9	3.3	2.9
Lube Oil, Wax, & Miscellaneous	1.2	None	None	None
<u>APPARENT PROCESSING GAIN</u>				
Vol% on Crude Input	6.4	6.4	7.0	6.4
<u>LPG INPUT</u>				
Vol% on Crude Input	1.0	1.2	0.8	1.2

Table 3-6. OVERALL REFINERY MATERIAL BALANCE - CASE 1

<u>INPUT</u>	<u>BPCD</u>	<u>#/H</u>	<u>SULFUR CONTENT, #/H</u>
Crude Oil	100,00	1,292,720	16,377
Purchased N-Butane	1,204	10,250	-
H ₂ Plant: Nat. Gas-FOE	848	10,020	-
Water		22,550	-
Total Input	<u>102,052</u>	<u>1,335,540</u>	
<u>OUTPUT</u>			
Gas to Fuel - FOE	3,769	46,210	182
H ₂ S to Sulfur Recovery	-	7,030	6,613
LPG	2,874	21,360	-
Gasolines	55,519	592,760	315
Alkylation By-product Oil	6	80	-
Jet Fuel & Kerosine	11,582	140,060	68
Diesel & Distillate Fuel Oil	14,787	182,400	472
No. 6 Fuel Oil	14,629	212,010	5,167
Asphalt	2,200	33,540	1,017
Delayed Coke (5 bbl = 1 Short Ton)	3,100	51,660	1,723
Catalytic Cracker Coke Burned	-	20,450	820
CO ₂ From H ₂ Plant	-	27,560	-
NH ₃ From Hydrocracker	-	420	-
Total	<u>108,466</u>	<u>1,335,540</u>	<u>16,377</u>
Apparent Gain	6,414		

Table 3-7. GASOLINE POOL - CASE I

	ISOBUTANE	N-BUTANE	LIGHT VIRGIN GASOLINE	LIGHT COKER GASOLINE	LIGHT VISBREAKER GASOLINE	REFORMATE	ALKYLATE	CAT CRACKED GASOLINE	LIGHT HYDRO-CRACKATE	HDS GASOLINE	TOTAL
TBP BOILING RANGE °F			C5-200	C5-200	C5-200	C5-EP	C5-EP	C5-430	C5-200	C5-400	
VOL FRACTION	0.003	0.075	0.108	0.017	0.002	0.359	0.090	0.263	0.081	0.002	1.000
BPCD	158	4.137	5.990	927	115	19,970	5,000	14,605	4,481	136	55,519
°API (SP GR)	(0.5626)	(0.584)	74.0	69.7	75.0	48.0	71.6	57.2	76.5	61.0	61.5
LB/H	1,290	35,210	60,060	9,490	1,150	229,340	50,740	159,620	44,410	1,450	592,760
REID VAPOR PRESSURE	82.5	59.1	9.0	6.7	6.5	3.5	3.1	6.7	12.0	7.0	10.0
OCTANE											
RESEARCH CLEAR	102.6	93.8	70.0	81.1	81	94.0	94.1	93.2	82.8	63	90.1
RESEARCH + 3 cc	104.2	101.6	88.2	88.3	88	100.0	105.1	98.2	96.5	84	98.4
MOTOR CLEAR	97.6	90.3	68.2	67.7	68	84.8	93.0	82.2	82.5	63	83.0
MOTOR + 3 cc	103.0	100.4	86.6	75.5	76	90.7	107.0	87.2	99.6	85	92.0
OLEFINS VOL %	-	-	3	37	37	1.0	---	17	---	---	5.4
AROMATICS VOL %	-	-	3	4	4	34	---	34	2	---	21.5
SULFUR WT %	-	-	0.019	0.49	0.04	-	---	0.158	-	-	0.053
LB/H	-	-	11	47	5	-	---	252	---	-	315

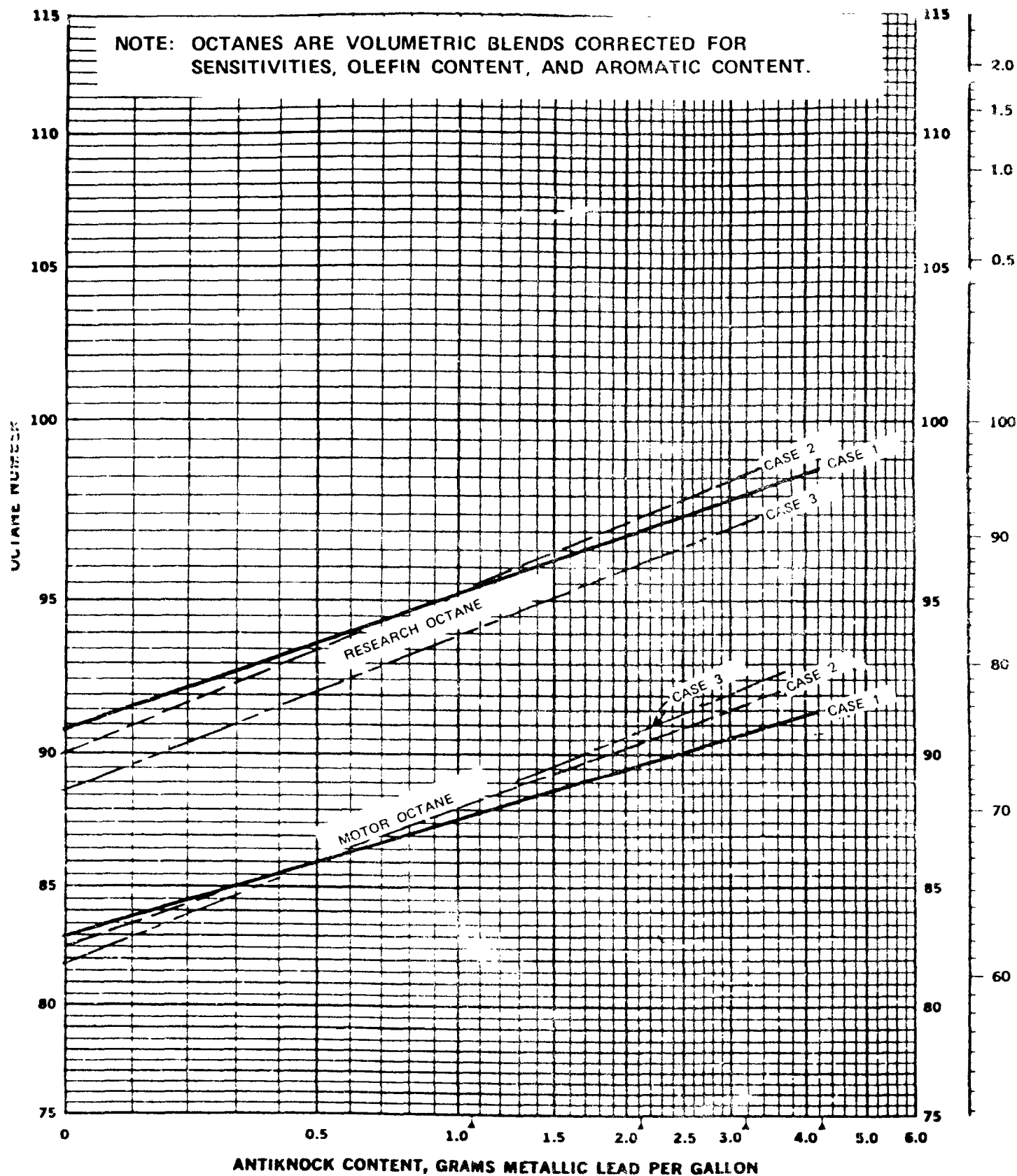


Figure 3-2. Octanes of Total Gasoline Pool

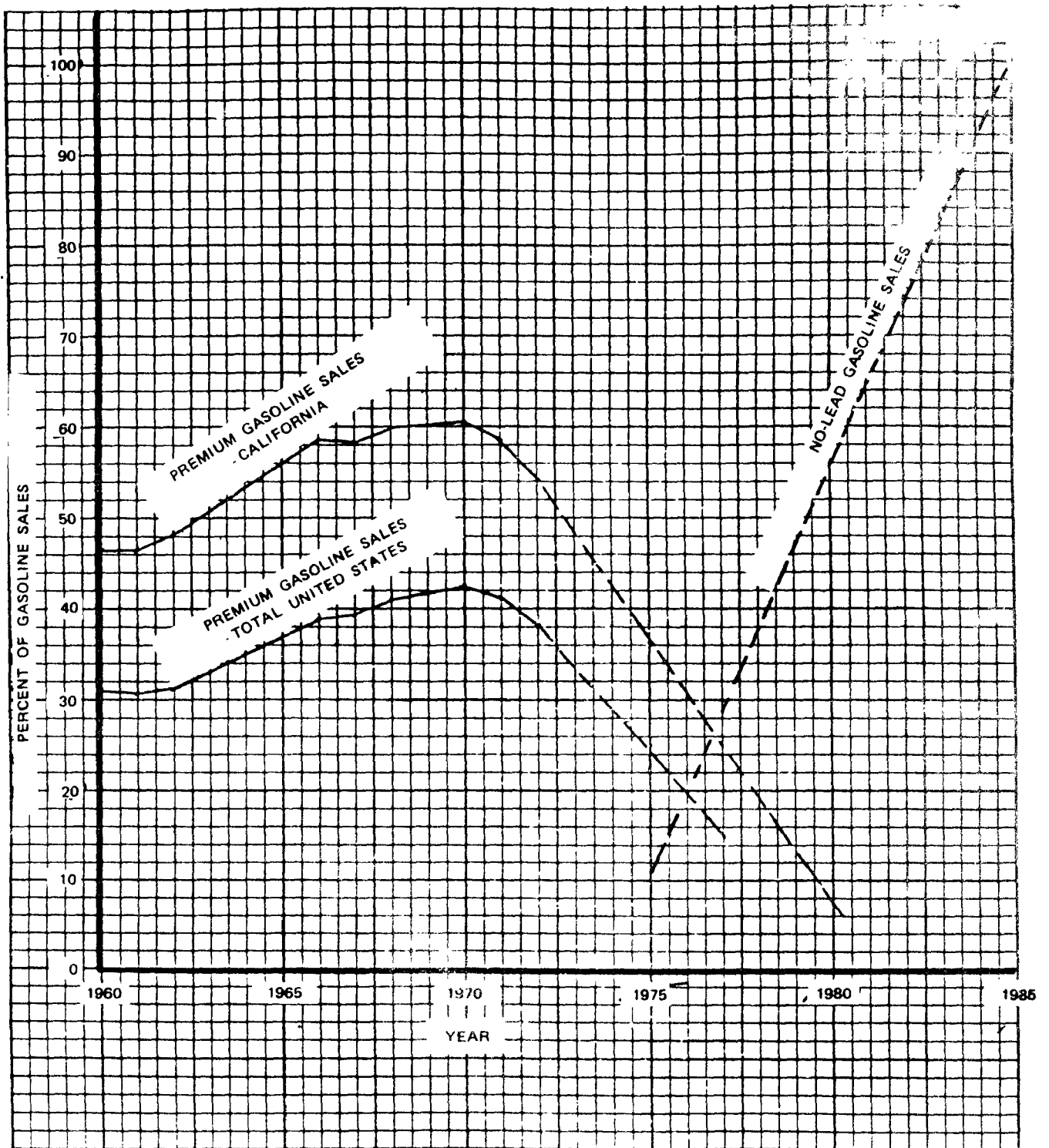


Figure 3-3. Projected Percent of Sales of Premium and No-Lead Gasoline in California.

compression cars are junked. The projected sales percent of no-lead gasoline is assumed to follow the projected sales of new cars which require no-lead gasolines.

PRODUCTION OF NO-LEAD, LOW-SULFUR GASOLINE IN PRESENT CALIFORNIA REFINERIES

The time to plan, finance, and construct refining facilities to upgrade gasoline blending components requires about three years from the date of a firm decision to proceed. During the period until the additional gasoline-upgrade facilities are onstream, the no-lead, low-sulfur gasolines will have to be blended from low-sulfur components which can be produced in the present refining facilities.

In the California refineries, the present low-sulfur gasoline components are normal butane, reformat, light hydrocrackate and alkylate.

The potential production of no-lead, low-sulfur gasoline together with premium and regular gasoline were calculated attempting to meet the EPA regulations on lead phase-down using the blending components produced in Case 1. The results (Table 3-8) indicate that the projected percent of gasoline sales can be met in 1975 and 1976. In 1977 and later years, the EPA limit on lead content would be exceeded.

No-lead gasoline and premium gasoline utilize the same gasoline blending components such as reformat and light hydrocrackate or alkylate. Regular gasoline will contain the lower-octane blending components which cannot be utilized in no-lead or premium gasoline blends. Therefore if the projected sales demand for no-lead or premium gasoline significantly increased from the projected sales, shortages of premium and no-lead gasoline may occur.

In 1977 and later years, octane up-grading will become necessary to meet the EPA regulations on lead phase-down. In 1977, it may be possible to increase the reformer severity. In the later years, new octane up-grading facilities will need to be installed. The processes for octane up-grading include isomerization of normal pentane and hexanes and reforming of heavy catalytic cracked naphtha.

In producing no-lead, low-sulfur gasoline, Table 3-8 shows that the sulfur contents by 1979 in the premium and regular gasolines will be about twice the present sulfur levels. In 1979, regular gasoline and premium gasoline would respectively contain 0.11 and 0.07 wt% sulfur.

Table 3-8. POTENTIAL GASOLINE PRODUCTION IN CASE 1
(1)
WITH LEAD PHASE-DOWN

Year	1972	1975	1976	1977	1978	1979
<u>Lead Content, Grams/Gal</u>						
Allowed by EPA	4.2 ⁽²⁾	1.7	1.4	1.0	0.8	0.5
Total Gasoline Pool	2.12	1.56	1.07	1.01	1.03	0.93
Premium Gasoline	2.65	2.91	2.00	2.07	2.75	3.00
Regular Gasoline	1.32	0.92	0.92	1.07	1.17	1.36
<u>Potential Gasoline, Vol%</u>						
No-Lead, Low-Sulfur (92 RON)	-	11	20	29	38	47
Premium (99.5 RON)	54	37	31	25	19	13
Regular (93.5 RON)	46	52	49	46	43	40
<u>No-Lead Gasoline, Vol%</u>						
N-Butane	-	9	9	9	9	9
Light Hydrocrackate	-	18	18	18	18	17
Reformate	-	73	73	73	73	70
Alkylate	-	-	-	-	-	4
<u>Premium Gasoline, Vol%</u>						
N-Butane	9	8	9	9	9	9
Alkylate	17	20	29	22	22	21
Reformate	40	33	26	31	31	24
FCC Gasoline	25	23	21	26	31	46
Light Hydrocrackate	9	16	15	12	7	-
<u>Regular Gasoline, Vol%</u>						
N-Butane	6	7	6	6	5	5
Isobutane	0.5	0.5	0.5	0.5	0.5	0.5
Light Coker & VB Gasoline	4	4	4	4	5	5
Reformate	31	30	27	15	5	-
FCC Gasoline	28	34	40	43	48	51
Light Hydrocrackate	7	-	-	-	-	-
Light Virgin Gasoline	23	21	22	23	25	27
HDS Gasoline	0.5	0.5	0.5	0.5	0.5	0.5
Alkylate	-	3	-	8	11	11

Table 3-8 (continued). POTENTIAL GASOLINE PRODUCTION IN CASE 1
(1)
WITH LEAD PHASE-DOWN

Year	1972	1975	1976	1977	1978	1979
<u>Gasoline Octanes</u>						
No-Lead, Research	-	92.4	92.4	92.4	92.4	92.5
Motor	-	85.0	85.0	85.0	85.0	85.2
Premium, Research	99.6	99.5	99.5	99.5	99.5	99.5
Motor	92.4	93.5	96.8	95.2	92.6	91.7
Regular, Research	93.9	93.5	93.5	93.5	93.5	93.5
Motor	86.3	85.5	84.9	85.7	85.8	85.9
<u>Sulfur, Wt%</u>						
No-Lead, Low-Sulfur	-	-	-	-	-	-
Premium	0.033	0.037	0.034	0.043	0.050	0.074
Regular	0.058	0.076	0.087	0.094	0.104	0.112
<u>Comment - See Note</u>				(3)	(3)	(3)

NOTES:

- (1) Gasoline blends are calculated at 10 pounds Reid vapor pressure using the gasoline components with the yields and properties from Case 1 for the "Average" of California refineries.
- (2) Legal limit was 4.2 grams lead content per gallon prior to EPA regulations.
- (3) In 1977, 1978 and 1979, the lead content in the total gasolines would exceed the EPA limits on lead content. Additional octane upgrading refining facilities will be required to meet the EPA limits on lead content.

CHAPTER 4

DESULFURIZATION OF GASOLINES

GENERAL

In order to calculate the costs of producing low-sulfur gasolines, the "Average of California Refineries" was taken as the basic refinery and then low-sulfur gasoline produced by two types of process additions:

- Hydrodesulfurization of catalytic cracker feedstock and hydrodesulfurization of the light virgin, light coker, and light visbreaker gasolines (Case 2).
- Hydrodesulfurization of catalytic cracker gasoline and hydrodesulfurization of the light gasolines (Case 3).

In this study, the costs were purposely made on the conservative (i. e. higher capital) side as follows:

- Investments included new units to provide the incremental capacities for hydrogen, amine treating and sulfur recovery. In Case 3, these units are small and may not be required.
- In Case 2, the catalytic cracker conversion was kept at 75% as in Case 1. Depending upon the whether the refinery catalytic cracker severity is coke limited or gas limited, it may be practical in Case 2 to increase the catalytic cracker conversion to make this case more attractive.

In Case 3, the octane of the catalytic cracked gasoline would be lower after hydrotreating due to partial olefin saturation. Economics debited the lower octane by penalizing the production of premium gasoline using the price differential between premium and regular gasolines. If additional octane up-grading were necessary the costs would further penalize Case 3.

CASE 2: AVERAGE CALIFORNIA REFINERY WITH HYDRODESULFURIZATION OF CATALYTIC CRACKER FEED AND LIGHT GASOLINES

In Case 2, the crude oil and refinery process units would be the same as Case 1 of the "Average of California Refineries" with the following additions:

- Hydrodesulfurization of catalytic cracker feedstock.
- Light gasoline hydrodesulfurization.
- New units for incremental needs for hydrogen, amine treating, and sulfur recovery.

The flow scheme for "Average of California Refineries" shows the added hydrodesulfurization unit. The yields and product properties are listed in Table 3-5 together with the information for the West Coast production and Case 1. For Case 2, the overall material balance

is shown in Table 3-9 and the gasoline pool is shown in Table 3-10. The sulfur content of the total gasolines would be 0.006 weight percent.

The incremental investment to produce low-sulfur gasolines is estimated to be 18.7 million dollars (Table 3-11) in Case 2 for a 100,000 bpcd refinery.

In California, there are eleven refineries which are larger than 75,000 bpsd. The crude capacities of these eleven refineries total 1,402,000 bpsd which is 78% of the total crude capacity of all refineries in California. If new facilities were installed to produce low-sulfur gasolines in these eleven refineries by desulfurizing light virgin gasoline, light thermal gasolines, and catalytic cracker feedstock (Case 2), an investment of about 250 million would be required based on May, 1974 costs.

Economics show that this desulfurization scheme would add 1.1 cents per gallon to the costs of producing gasoline (Table 3-16).

The potential production of no-lead, premium and regular gasolines were calculated attempting to meet the EPA regulations on lead phase-down using the blending components produced in Case 2. All the gasolines would be low-sulfur. The results (Table 3-12) indicate that the projected percent of gasoline sales can be met in 1976. In 1977 and later years, the EPA limit on lead content would be exceeded.

Results in Table 3-16 for Case 2 and in Table 3-8 for Case 1 indicate that refiners should start planning installation of new octane up-grading facilities or that EPA should relax the lead phase-down regulations to about the 1.4 grams per gallon for 1976 and later years.

CASE 3: AVERAGE CALIFORNIA REFINERY WITH HYDRODESULFURIZATION OF CATALYTIC CRACKED GASOLINE AND LIGHT GASOLINES

In Case 3, the crude oil and refinery process units would be the same as Case 1 of the "Average of California Refineries" with the following additions:

- Hydrodesulfurization of catalytic cracked gasoline.
- Light gasoline hydrodesulfurization.
- New units for incremental needs for hydrogen, amine treating, and sulfur recovery.

Table 3-9. OVERALL REFINERY MATERIAL BALANCE - CASE 2

<u>INPUT</u>	<u>BPCD</u>	<u>#/H</u>	<u>SULFUR CONTENT, #/H</u>
Crude Oil	100,000	1,292,720	16,377
Purchased N-Butane	796	6,770	
H ₂ Plant: Nat. Gas-FOE	1,076	12,720	
Water		28,620	
Total	101,872	1,340,830	16,377
<u>OUTPUT</u>			
Gas to Fuel - FOE	3,746	46,120	183
H ₂ S to Sulfur Recovery		9,670	9,100
LPG	3,335	24,860	
Gasoline	55,536	589,360	36
Alkylation	5	70	
Jet Fuel & Kerosine	11,582	140,060	68
Diesel & Distillate Fuel Oil	14,821	182,860	473
No. 6 Fuel Oil	14,587	210,660	3,673
Asphalt	2,200	33,540	1,017
Delayed Coke (5 bbl=1 Short Ton)	3,100	51,660	1,723
Catalytic Cracker Coke			
Burned		16,070	104
CO ₂ From H ₂ Plant		34,980	
NH ₃ From Hydrocracker		420	
Total	108,812	1,340,830	16,377
Apparent Gain	7,040		

Table 3-10. GASOLINE POOL - CASE 2

TBP BOILING RANGE OF		ISOBUTANE	N-BUTANE	HDS LIGHT GASOLINE	REFORMATE	ALKYLATE	CAI CRACKED GASOLINE	LIGHT HYDRO- CRACKATE	HDS GASOLINES	TOTAL
				C5-200	C5-EP	C5-EP	C5-430	C5-200	C5-EP	
VOL FRACTION		0.006	0.068	0.127	0.359	0.090	0.264	0.081	0.005	1.000
BPCD		316	3,793	7,040	19,970	5,000	14,678	4,481	258	55,536
% API (SP GR)		(0.5626)	(0.584)	73.6	48.0	71.4	58.6	76.5	61.2	62.6
LB/H		2,580	32,280	70,750	229,340	50,800	156,940	44,410	2,760	589,860
REFID VAPOR PRESSURE		82.5	50.1	8.7	3.5	3.2	7.1	12.0	7.0	10.0
OCTANE										
RESEARCH CLEAR		102.6	93.8	68.7	94.0	94.3	91.9	82.8	63	89.3
RESEARCH + 3 cc		104.2	101.6	88.3	100.0	105.4	99.2	96.8	84	98.6
MOTOR CLEAR		97.6	90.3	67.1	84.8	93.3	81.0	82.5	63	82.5
MOTOR + 3 cc		103.0	100.4	87.0	90.7	107.3	88.3	99.6	85	92.5
OLEFINS, VOL %					1.0		15.6	---		4.5
AROMATICS, VOL %				3.1	34		32	2		21.3
SULFUR, WT %				0.004			0.02			0.006
LB/H				3			33			36

Table 3-11. INVESTMENT FOR DESULFURIZATION FACILITIES - CASE 2

<u>FACILITY</u>	<u>CAPACITY</u>	<u>INVESTMENT, *</u> <u>MILLION DOLLARS</u>
Refinery Size	100,000 BPCD	-
Light Gasoline Hydrodesulfurizer	7,400 BPSD	3.2
Catalytic Cracker Feed Hydrodesulfurizer	25,700 BPSD	6.2
Amine H ₂ S Removal	Amine Circulation 193 GPM	1.0
Sulfur Recovery (Claus Plant)	30 Short Tons/Day	0.5
Hydrogen Plant	8.3 MM SCF/D	<u>3.5</u>
Onsite		14.4
Offsite (at 30% of Onsite)		4.3
Total Investment		<u><u>18.7</u></u>

* Investment includes paid-up royalties (if applicable) plus initial charges of catalysts. Investment at May, 1974 levels.

Table 3-12. POTENTIAL GASOLINE PRODUCTION IN CASE 2
WITH LEAD PHASE-DOWN⁽¹⁾

Year	1976	1977	1978	1979
<u>Lead Content, Grams/Gal</u>				
Allowed By EPA	1.4	1.0	0.8	0.5
Total Gasoline Pool	1.24	1.03	0.93	0.76
Premium Gasoline	2.41	2.28	2.38	1.87
Regular Gasoline	1.00	1.00	1.11	1.28
<u>Potential Gasoline, Vol%</u>				
No-Lead, Low-Sulfur (92 RON)	20	29	38	47
Premium (99.5 RON)	31	25	19	13
Regular (93.5 RON)	49	46	43	40
<u>No-Lead Gasoline, Vol%</u>				
N-Butane	8	9	9	9
Light Hydrocrackate	13	18	18	17
Reformate	38	73	73	72
FCC Gasoline	28	-	-	2
Alkylate	13	-	-	-
<u>Premium Gasoline, Vol%</u>				
N-Butane	8	7	9	9
Alkylate	12	22	22	35
Reformate	41	15	29	16
FCC Gasoline	30	44	33	40
Light Hydrocrackate	9	12	7	-
<u>Regular Gasoline, Vol%</u>				
N-Butane	5	5	4	3
Isobutane	1	1	1	1
HDS Light Gasoline	26	28	30	32
Reformate	32	24	6	-
Alkylate	5	8	11	10
Catalytic Cracked Gasoline	24	33	47	53
Light Hydrocrackate	6	-	-	-
HDS Gasoline	1	1	1	1

Table 3-12 (continued). POTENTIAL GASOLINE PRODUCTION IN CASE 2
WITH LEAD PHASE-DOWN⁽¹⁾

Year	1976	1977	1978	1979
<u>Gasoline Octanes</u>				
No-Lead, Research Motor	92.3 84.6	92.4 85.1	92.4 85.1	92.5 85.1
Premium, Research Motor	99.5 91.5	99.5 92.2	99.5 92.5	99.5 92.9
Regular, Research Motor	93.5 86.7	93.5 86.3	93.5 86.5	93.5 85.8
<u>Sulfur, Wt%</u>				
No-Lead, Low-Sulfur	0.006	0.000	0.000	0.000
Premium	0.006	0.010	0.007	0.009
Regular	0.006	0.008	0.011	0.013
<u>Comments - See Note</u>		(2)	(2)	(2)

NOTES:

- (1) Gasoline blends are calculated at 10 pounds Reid vapor pressure using the gasoline components in Case 2.
- (2) In 1977, 1978 and 1979, the lead content in the total gasolines would exceed the EPA limits on lead content. Additional octane upgrading refining facilities will be required to meet the EPA limits on lead content.

Table 3-13. OVERALL REFINERY MATERIAL BALANCE - CASE 3

<u>INPUT</u>	<u>BPCD</u>	<u>#/H</u>	<u>SULFUR CONTENT, #/H</u>
Crude Oil	100,000	1,292,720	16,377
Purchased N-Butane	1,176	10,010	-
H ₂ Plant: Nat. Gas- FOE	929	10,980	-
Water	-	24,710	-
Total	<u>102,105</u>	<u>1,338,420</u>	<u>16,377</u>
<u>OUTPUT</u>			
Gas to Fuel-FOE	3,769	46,210	182
H ₂ S to Sulfur Recovery	-	7,320	6,892
LPG	2,874	21,360	-
Gasoline	55,533	592,710	36
Alkylation By-Product Oil	6	80	-
Jet Fuel & Kerosine	11,582	140,060	68
Diesel & Distillate Fuel Oil	14,787	182,400	472
No. 6 Fuel Oil	14,629	212,010	5,167
Asphalt	2,200	33,540	1,017
Delayed Coke (5 bbl= 1 Short Ton)	3,100	51,660	1,723
Catalytic Cracker Coke Burned	-	20,450	820
CO ₂ From H ₂ Plant	-	30,200	-
NH ₃ From Hydrocracker	-	420	-
Total	<u>108,480</u>	<u>1,338,420</u>	<u>16,377</u>
Apparent Gain	6,375		

Table 3-14. GASOLINE POOL - CASE 3

	ISOBUTANE	N-BUTANE	HDS LIGHT GASOLINE	REFORMATE	ALKYLATE	HDS CAT CRACKED GASOLINE	LIGHT HYDRO- CRACKATH	HDS GASOLINE	TOTAL
1 BT BOILING RANGE OF			C5-200	C5-EP	C5-EP	C5-430	C5-200	C5-400	
VOL FRACTION	0.003	0.074	0.127	0.359	0.090	0.264	0.081	0.002	1.000
BPCD	158	4.109	7.040	19.970	5.000	14.639	4.481	136	55.533
API (SP GR)	(0.5626)	(0.564)	73.6	48.0	71.6	57.4	76.5	61.0	61.6
1 B/H	1.290	34.970	70.750	229.340	50.746	159.760	44.410	1.450	592.710
FLUID VAPOR PRESSURE	82.5	59.1	8.7	3.5	3.1	6.7	12.0	7.0	10.0
OCTANE									
RESEARCH CLEAR	102.6	93.8	68.7	94.0	94.1	87.6	82.8	63	88.14
RESEARCH + 3 CC	104.2	101.6	86.3	100.0	105.1	94.0	96.8	84	97.23
MOTOR CLEAR	97.6	90.3	67.1	84.8	93.0	78.3	82.5	63	81.79
MOTOR + 3 CC	103.0	100.4	87.0	90.7	107.0	89.3	94.6	85	92.79
OLEFINS, VOL %			--	1.0		7.7	--		2.4
AROMATICS, VOL %			3.1	34		34	2		21.7
SULFUR WT %			0.004			0.021			0.006
1 B/H			3			33			36

The yields and product properties for Case 3 are listed in Table 3-5 together with the information for the West Coast production and Cases 1 and 2.

In removing sulfur from catalytic cracked gasoline, 87% desulfurization was selected since this yields about the same sulfur content in the total gasolines as in Case 2 (0.006 wt% sulfur). At this desulfurization severity, 55% of the olefins in the catalytic cracked gasolines would be hydrogenated and lower the octane. In the economics, the lower octane shows a penalty of 0.1 cent per gallon of gasoline for 0.3 octane (Research/2+Motor/2) difference at 1.0 gram lead per gallon.

In Case 3, the incremental investment to produce low-sulfur gasolines is estimated to be 13.5 million dollars (Table 3-15) for a 100,000 bpcd refinery. Economics show that this desulfurization scheme would add 1.0 cents per gallon to the costs of producing gasoline (Table 3-16).

SULFUR DISTRIBUTION IN REFINERY PRODUCTS AND EMISSIONS

Sulfur contained in the crude oil to the refinery is distributed in the products, recovered as elemental sulfur, and emitted as SO₂ to the atmosphere as shown in Table 3-17.

In Case 1, the sulfur in the crude oil is distributed 37.8% to residual fuel oil and asphalt, 38.0% recovered as elemental sulfur and 8.5% emitted as SO₂ to the atmosphere. By desulfurizing the catalytic cracker feedstock in Case 2, the recovery of elemental sulfur can be increased to 52.3% and the emission decreased to 5.1%.

DISCUSSION

This study was based on a refinery model which represents an average of the refineries in California. However, each refinery in California may be distinctly different from this refinery model in both the process units, crude mix charged, operating conditions and products. Each refinery bases its operations on market demands, availability of crudes, limitations of process units, and flexibility of operating conditions. If it becomes mandatory to produce only low-sulfur gasolines, each California refinery should prepare their own economics as to which process scheme best suits its refinery or refineries.

It is believed that desulfurization of the catalytic cracker feed will generally be the most attractive.

Table 3-15. INVESTMENT FOR DESULFURIZATION - CASE 3

<u>FACILITY</u>	<u>CAPACITY</u>	<u>INVESTMENT, MILLION DOLLARS</u>
Refinery Size	100,000 BPCD	-
Light Gasoline Hydrodesulfurizer	7,400 BPSD	3.2
FCC Gasoline Hydrodesulfurizer	15,400 BPSD	4.4
Amine H ₂ S Removal	Amine Circulation 19 GPM	0.3
Sulfur Recovery (Claus Plant)	3.5 Short Tons/Day	0.1
Hydrogen Plant	4.0 MM SCF/D	<u>2.4</u>
Onsite		10.4
Offsite (at 30% of Onsite)		3.1
Total Investment		<u><u>13.5</u></u>

* Investment includes paid-up royalties (if applicable) plus initial charges of catalysts.

Table 3-16. COSTS FOR GASOLINE DESULFURIZATION*

Case	<u>2</u>	<u>3</u>
Refinery Capacity, BPCD	100,000	100,000
Investment for Gasoline Desulfurization, Million Dollars	18.7	13.5
Years to Payout	5	5
Return, Percent Per Year	20	20
Million Dollars Per Year:		
Cash Flow	3.74	2.70
Depreciation	1.05	0.90
Income After Tax	2.69	1.80
Income Tax at 48%	2.48	1.66
Tax Base	5.17	3.46
Operating Costs:		
Depreciation	1.05	0.90
Operating Manpower	0.33	0.33
Utilities	3.10	1.45
Catalyst Replacement	0.14	0.04
Interest	0.94	0.68
Maintenance	0.66	0.48
Local Taxes & Insurance	0.28	0.20
Incremental Product Credits	-2.28	0.15
Debit for Lower Gasoline Octane	-	0.85
Total Operating Costs	<u>4.22</u>	<u>5.08</u>
Total added Costs for Gasoline Desulfurization: Million Dollars Per Year (Tax Base + Oper. Costs)	9.39	8.54
Cents Per Gallon Gasoline	1.10	1.00

* Incremental costs above Case 1.

Table 3-17. SULFUR DISTRIBUTION IN REFINERY PRODUCTS AND EMISSIONS

	<u>SULFUR DISTRIBUTION, % *</u>		
	<u>Case 1</u>	<u>Case 2</u>	<u>Case 3</u>
Gasoline	1.9	0.2	0.2
Jet Fuel & Kerosine	0.4	0.4	0.4
Diesel & Distillate Fuel Oil	2.9	2.9	2.9
No. 6 Fuel Oil	31.6	22.4	31.6
Asphalt	6.2	6.2	6.2
Delayed Coke	10.5	10.5	10.5
Recovered as Elemental Sulfur	38.0	52.3	39.6
Emitted as SO ₂ to Atmosphere	<u>8.5</u>	<u>5.1</u>	<u>8.6</u>
Total	100.0	100.0	100.0

* As percent of sulfur in crude oil.

Table 3-18. REFINERY RUNS - PAD DISTRICT 5 (WEST COAST)

Basis: Bu Mines Statistics for January, 1972 through September, 1973.

<u>INPUT</u>	<u>MILLION BARRELS</u>	<u>VOL% ON CRUDE INPUT</u>
Crude Oil - Total	1,222	100.0
U. S.	757	61.9
Foreign	465	38.1
Natural Gas Liquids - Total	35	2.9
LPG	12	1.0
Nat. Gas.	<u>23</u>	<u>1.9</u>
Total Input	1,257	102.9
<u>OUTPUT</u>		
Gasoline (1)	623	51.0
Liquefied Refinery Gas (2)	30	2.5
Jet Fuel and Kerosine (3)	134	11.0
Diesel and Distillate Fuel Oil	167	13.7
Residual Fuel Oil	213	17.4
Lube Oil and Wax	11	0.9
Coke (5 bbls = 1 short ton)	55	4.5
Asphalt and Road Oil	40	3.3
Still Gas to Fuel	58	4.7
Miscellaneous	<u>4</u>	<u>0.3</u>
Total Output	1,335	109.3
Processing Gain	78	6.4

NOTES:

- (1) Includes motor gasolines, aviation gasolines, petrochemical feedstocks (aromatics) and special naphthas.
- (2) Includes ethylene-ethane and liquefied refinery gas for fuel and chemical uses.
- (3) Includes jet fuel (kerosine type) and 50% of naphtha-type jet fuel.

Table 3-19. AVERAGE PROPERTIES OF PRODUCT
SALES IN SOUTHERN CALIFORNIA

	REGULAR GASOLINE	PREMIUM GASOLINE	REGULAR GASOLINE	PREMIUM GASOLINE	AVERAGE TOTAL GASOLINE	KEROSENE	JET A FUEL	DIESEL FUEL (TRUCKS TRACTORS)	NO. 2 FURNACE OIL	NO. 6 FUEL OIL
BUREAU MONTHLY SURVEY	WINTER 1972-1973	WINTER 1972-1973	SUMMER 1973	SUMMER 1973				1973	1973	1973
GRAVITY °API	59.2	58.4	58.5	58.2	58.5	41.7	42.9	35.3	34.5	11.0
ASTM DISTILLATION °F										
IBP	87	86	93	92		239	331	395	388	
10	113	115	124	126		370	369	453	446	
30	159	167	166	173						
50	209	219	212	219		412	415	520	519	
70	269	264	270	263						
90	346	324	342	327		469	473	600	602	
EP	412	403	412	409		516	512	643	647	
SULFUR, WT %	0.069	0.061	0.046	0.034	0.046	0.073	0.045	0.32	0.22	1.50
ANILINE POINT, °F						138	143	149	146	
CETANE NUMBER (INDEX)								47.3 (50.7)	49.0	
SMOKE POINT, MIN							23.3			
VISCOSITY, CS AT 100°F								2.95	3.20	
VISCOSITY, FUROL AT 122°F										159
CARBON RESIDUE, WT %										11.2
LEAD, g/gal	1.24	2.64	1.40	2.65	2.12					
OCTANE NUMBER										
RESEARCH	83.6	99.9	93.3	99.1	97.2					
MOTOR	85.2	91.6	85.2	91.2	89.0					
(RESEARCH + MOTOR)/2	89.5	95.8	89.3	95.2	93.1					
REID VAPOR PRESSURE	11.1	11.0	8.9	9.0	10.0					
SALES, %	37	63	42	58						

APPENDIX A
SURVEY OF REFINERIES
IN CALIFORNIA

CALIFORNIA

Company and location	Crude capacity b/cd	Vacuum distillation b/sd	Thermal op- erations	Cat cracking Fresh feed	Charge capacity b/sd	Cat reforming	Cat hydro- cracking	Cat hydro- refining	Cat hydro- treating	Alkyl- ation	Production capacity—b/sd Aromatics- Isomerization	Lubes	Asphalt	Coke (t/d)
Atlantic Richfield Co.—Carson	165,000	173,000	93,000	123,000 137,000 25,500	157,000	8,000	132,000	117,000	132,000	17,200	12,490 13,000			1,650
Beacon Oil Co.—Hanford	12,000	12,100		25,500 1,500 2,750 49,650			11,650		18,000					
Champion Petroleum Co.—Wilmington	28,750	30,000	18,600											
Carson Oil Co. (Leased from Golden Eagle Refining Co.)—Torrance	6,900	7,000												
Douglas Oil Co. of California— Paramount	35,000	36,000	21,000											
Santa Maria	8,200	8,500	7,500											
Edgington Oil Co.—Long Beach	15,000	16,000												
Edgington Orndorf Refinery—Orndorf	NR	2,500												
Exxon Co.—Benicia	86,000	95,000	47,000	23,000	146,000	9,300	224,000	24,000	22,500	112,000				
Fletcher Oil & Refining Co.—Carson	15,200	16,000												
Golden Bear Division, Witco Chemical Corp.—Oildale	9,350	9,500	9,500											
Gulf Oil Co.—Santa Fe Springs	49,800	52,000	21,900	23,800	113,500	300	119,000	111,000	112,000	23,000		4,000	3,200 4,000	
Kern County Refinery Inc.— Bakersfield	12,000	13,500	5,000	6,000			23,000		13,500					
Lundberg-Tharald Oil Co.—South Gate	5,000	5,200	3,000											
Macmillan King-Free Oil Co. Inc.— Signal Hill	10,000	10,000												
Mobil Oil Corp.—Torrance	123,500	130,000	95,000	216,000 46,640	156,000	None	117,500 118,500	118,000	123,000 115,000 23,000	210,500				2,800
Mohawk Petroleum Corp. Inc.— Bakersfield	17,000	17,500												
Newhall Refining Co. Inc.—Newhall	NR	6,500	3,000											
Phillips Petroleum Co.—Avon	110,000	NR	74,500	142,000	147,000	NR	132,500	122,000	234,500	110,500	2,700	1,670		
Powerline Oil Co.—Santa Fe Springs	28,500	30,000	14,000		110,000	1,000	16,300	12,200	17,000	23,300			5,000	1,200
San Joaquin Refining Co.—Oildale	17,000	18,000	7,000						115,400				3,360	
Sequoia Refining Corp.—Hercules	27,000	28,300	5,900		146,000	40,000	225,000	118,000	216,000	16,600		4,500	10,400	
Shell Oil Co.—Martinez	100,000	103,000	56,600						115,000 116,000 111,000 111,000 230,000 233,000 11,000					
Wilmington	86,000	88,000	60,000	230,000	135,000	5,000	21,000		18,600	18,600	43,800			1,800
Standard Oil Co. of California— Bakersfield	NR	26,000		29,000										
El Segundo	NR	220,000	103,000	50,000	140,000	15,000	15,000	145,000	15,000	15,400	11,500		1,100 8,300	2,200
Richmond	NR	190,000	150,000		140,000	15,000	169,000	168,000	118,000	18,500	11,500 42,000	10,000	11,000	
Sunland Refining Corp.—Bakersfield	8,500	NR												
Tenneco—Bakersfield	1,200	NR												
Tosco Inc.—Wilmington	77,000	NR		48,000	128,000	NR	135,000	120,000	133,000	14,400	41,200			1,650
Tosco Petro Corp.—Bakersfield	26,500	27,000	17,000	6,000	110,000	2,000	112,500	112,000	15,000	11,800				180
Union Oil Co. of California— Los Angeles	104,000	107,000	83,000	20,000	45,000	7,000	229,000	21,000	137,000	18,000			10,000	
San Francisco	95,000	99,000	38,500	42,500			226,000	130,000	231,000 23,000 714,000			3,600	6,150	1,850
West Coast Oil Co.—Oildale	12,700	13,000	22,000										2,000	
Total**	1,714,900	1,796,700	936,000	456,640	476,600	126,000	472,650	314,300	651,800	89,300	28,290	23,770	92,110	14,955

LEGEND

Processes in table are

identified by numbers

Cat Hydrotreating

1. Residual desulfurizing
2. Heavy gas-oil desulfurizing
3. Residual visbreaking
4. Cat cracker and cycle stock feed pretreatment
5. Middle distillate
6. Other

Cat Hydrotreating

1. Pretreating cat-reformer feeds
2. Naphtha desulfurizing
3. Naphtha olefin or aromatics saturation
4. Straight-run distillate
5. Lube oil "polishing"
6. Other distillates
7. Other

Aromatics/Isomerization

1. BTX
2. Hydrodealkylation
3. Cyclohexane
4. C₄ feed
5. C₅ feed
6. C₅ and C₆ feed

Cat Reforming

Semiregenerative:

1. Conventional catalyst
2. Bimetallic catalyst

Cyclic:

3. Conventional catalyst
4. Bimetallic catalyst

Other:

5. Conventional
6. Bimetallic

Thermal Process

1. Gas-oil cracking
2. Visbreaking
3. Fluid coking
4. Delayed coking
5. Other

Alkylation

1. Sulfuric acid
2. Hydrofluoric acid

Cat Cracking

1. Fluid
2. Thermofor
3. Houdrflow

NR—Not reported

Cat Hydrocracking

1. Distillate upgrading
2. Residual upgrading
3. Lube-oil manufacturing
4. Other

*Diesel and jet. †Gasoline. ‡Turbine fuel. §Jet. ¶All figures are calendar day. Stream-day figures not reported. †Turbine aromatics saturation. **State totals include figures connected to stream-day or calendar-day basis. Cat cracking recycle total includes figures not reported (with recycle estimated at 30% of fresh feed).

APPENDIX B

SOURCES OF INFORMATION

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-----January 28, 1974

"Where District 5 Now Gets Crude, Products"

-----March 18, 1974

(Please read instructions on the reverse before completing)

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16. ABSTRACT

This report constitutes the first Annual Report of the ORD Catalyst Research Program required by the Administrator as noted in his testimony before the Senate Public Works Committee on November 6, 1973. It includes all research aspects of this broad multi-disciplinary program including: emissions characterization, measurement method development, monitoring, fuels analysis, toxicology, biology, epidemiology, human studies, and unregulated emissions control options. Principal focus is upon catalyst-generated sulfuric acid and noble metal particulate emissions.

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