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EVALUATION OF FUEL-CYCLE EMISSIONS ON A REACTIVITY BASIS

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ABSTRACT

Emissions associated with the production and distribution of conventional and alternative fuels can be significant in comparison with tailpipe and exhaust emissions. Examining these fuel-cycle emissions for alternative-fueled vehicles appears relevant when assessing the overall environmental impact of these vehicles from both a global and local perspective.

This study investigates these fuel-cycle emissions from the following fuels:

- Conventional gasoline (available in 1990)
- Phase 2 reformulated gasoline (RFG)
- Diesel
- Liquefied petroleum gas (LPG) from crude oil
- Methanol (M85 and M100) from natural gas
- M85 from biomass
- Ethanol (E85)
- Compressed natural gas (CNG)
- Liquefied natural gas (LNG)
- Hydrogen
- Electricity

This study determined oxides of nitrogen, non-methane organic gases (NMOG), methane, carbon monoxide, and carbon dioxide emissions. Reactivity adjusted NMOG emissions were a principal focus of this study. The reactivity effect of NMOG plus methane emissions is represented as an ozone potential calculated from the California Air Resources Board's (ARB's) reactivity factors. Emissions considered in this study are those associated with the operation of extraction, production, and distribution equipment. Emissions associated with the production or decommissioning of facilities or vehicles were not evaluated. Emission calculations are based on vehicle operation in the South Coast Air Basin; and the fuel-cycle emissions are allocated according to where they occur, including a summation of emissions within only the South Coast Air Basin.

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SUMMARY

Emissions associated with the production and distribution of conventional and alternative fuels can be significant in comparison with tailpipe and exhaust emissions. Examining these fuel-cycle emissions for alternative-fueled vehicles appears relevant when assessing the overall environmental impact of these vehicles from both global and local perspectives.

This study investigated fuel-cycle emissions from the following fuels:

- Conventional gasoline (available in 1990)
- Phase 2 reformulated gasoline (RFG)
- Diesel
- Liquefied petroleum gas (LPG) from crude oil
- Methanol (M85 and M100) from natural gas
- M85 from biomass
- Ethanol (E85)
- Compressed natural gas (CNG)
- Liquefied natural gas (LNG)
- Hydrogen
- Electricity

This study determined NO_x , non-methane organic gases (NMOG), methane, CO, and CO_2 emissions. The photochemical reactivity of NMOG emissions was a principal focus of this study. The reactivity effect of NMOG plus methane emissions is represented as an ozone potential calculated from ARB's reactivity factors. The emissions that were considered in this study are those associated with the operation of extraction, production, and distribution equipment. Emissions associated with the production or decommissioning of facilities or vehicles were not evaluated. Emission calculations are based on vehicle operation in the South Coast Air Basin and the fuel-cycle emissions are allocated according to where they occur, including a summation of emissions within only the South Coast Air Basin.

Fuel-cycle emissions vary substantially, based on factors such as the timeframe under consideration, vehicle fuel economy, the degree of emission control, amount of fuel produced and processed within the South Coast Air Basin, and assumptions regarding feedstock sources. Another important consideration is whether average emissions (total emissions divided by total fuel consumption), are relevant for policy decisions. Marginal emissions for the production of the last unit of fuel may be more relevant. This study considered average emissions in the 1990 and 2010 timeframes and marginal emissions in 2010. Except for hydrogen and electricity, this study is based on the operation of conventional internal-combustion-engine-powered light-duty vehicles. Electric vehicles are based on battery operation; and it is assumed that hydrogen vehicles will be fuel-cell-powered in 2010.

S.1 AVERAGE FUEL-CYCLE EMISSIONS

Figures S-1 through S-6 show the average fuel-cycle NO_x and NMOG emissions for the year 2010. Emissions were estimated over four scenarios. Scenario 1 represents emissions in the early 1990s and does not reflect large volume distribution. Scenarios 2, 3, and 4 reflect fuel production in 2010 with emission control and fuel economy assumptions that result in decreasing emissions. The emissions are grouped by the following categories:

- Extraction (includes feedstock extraction and transport)
- Production
- Marketing (includes fuel storage at processing and bulk storage, transportation, transmission, transport to fueling stations, and gaseous fuel compression energy)
- Distribution (local fuel station emissions)

Gasoline production and distribution result in higher average NO_x emissions than alternative-fuel production and distribution (except for electricity), since petroleum is refined in the South Coast Air Basin. The average fuel-cycle NO_x emissions from electric power production for electric vehicles are about the same as the fuel-cycle emissions from gasoline.

Average NMOG emissions for alternative fuels are lower than those of gasoline. The lower vapor pressure of alcohol fuels results in a slight reduction in NMOG compared with gasoline. LNG and LPG are assumed to be low-vapor-loss/spill-free operations by 2010 due to EPA regulatory requirements. CNG NMOG emissions consist primarily of distribution losses associated with existing pipelines. These emissions are not expected to increase with increased natural gas usage associated with CNG vehicles. NMOG emissions from electric power generation in the South Coast Air Basin include both combustion emissions and emissions associated with pipeline transport and storage. The emissions associated with natural gas distribution to power plants should not increase with additional power generation.

NMOG emissions from LPG distribution and fueling in Scenario 1 are very high due to vapor releases from fuel transfer operations. Vapor controls are assumed to be implemented to comply with emission regulations. Improvements in technology should reduce NMOG emissions to levels below those of conventional fuels.

Figures S-7 and S-8 show the ozone potential for average fuel production in the South Coast Air Basin for Scenario 3.

The low vapor pressure and ozone potential of methanol and ethanol suggest that the ozone potential from M85 and E85 distribution might be lower than that of gasoline. However, blending with gasoline and increased volumetric fuel consumption result in an ozone potential for distribution emissions somewhat lower than that of reformulated gasoline. Distribution emissions for E85 and M85 result in a maximum incremental reactivity (MIR) ozone potential of about 0.5 g O_3 /mi, which is about two-thirds that of gasoline. The ozone potential from vehicles powered by gaseous fuels, M100, diesel, and electricity are the lowest.

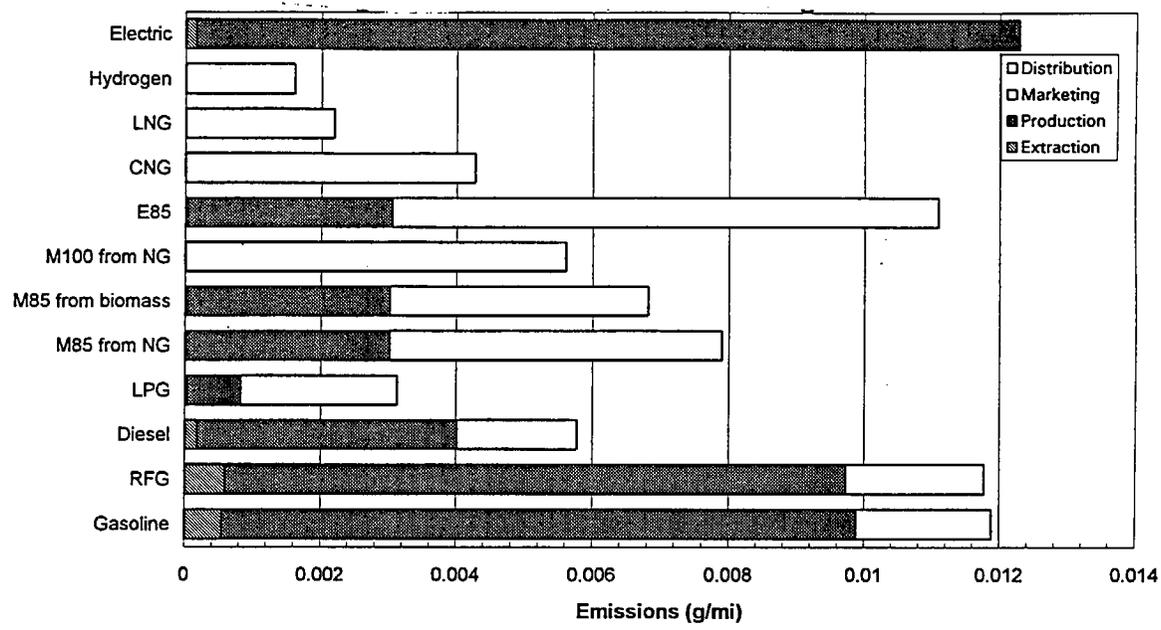


Figure S-1. Average NO_x, Scenario 2, South Coast (g/mi)

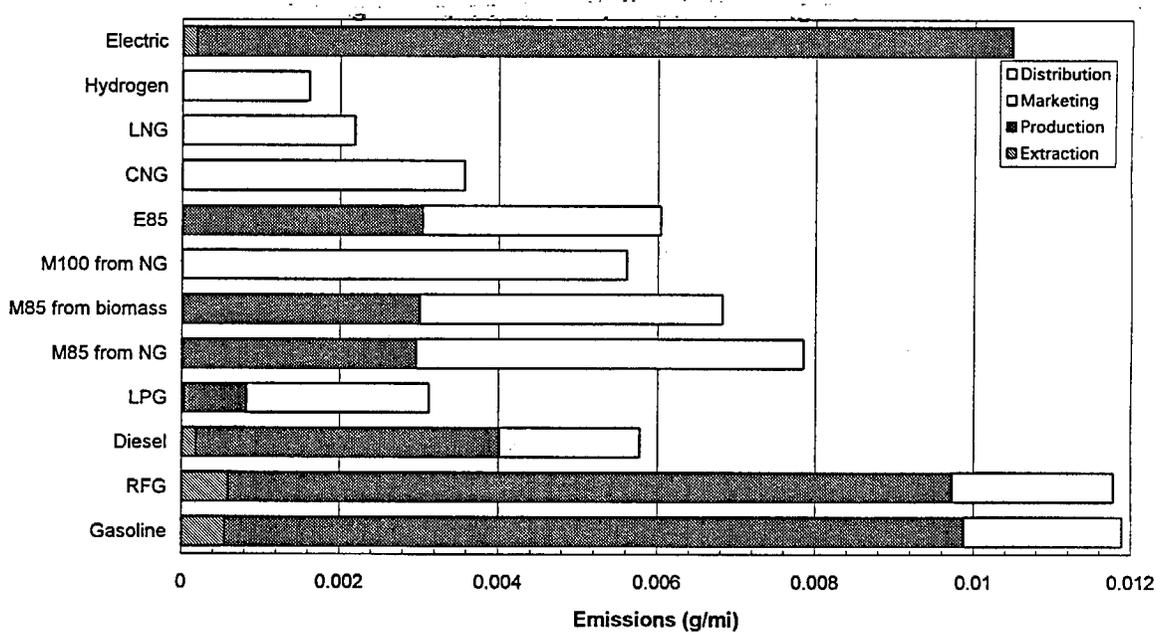


Figure S-2. Average NO_x, Scenario 3, South Coast (g/mi)

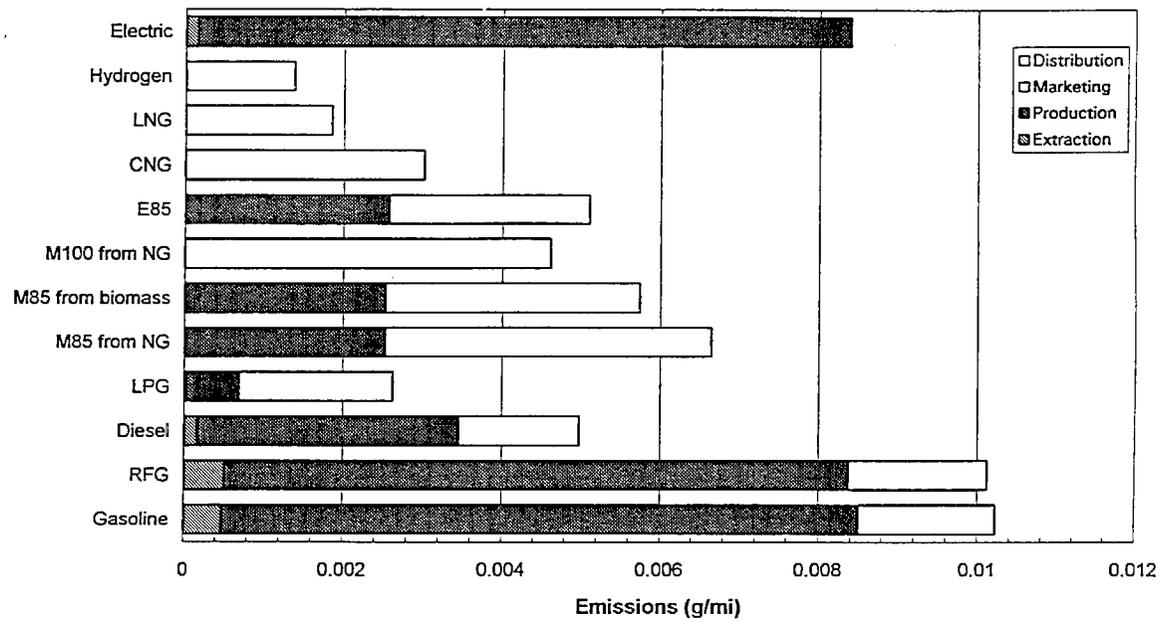


Figure S-3. Average NO_x, Scenario 4, South Coast (g/mi)

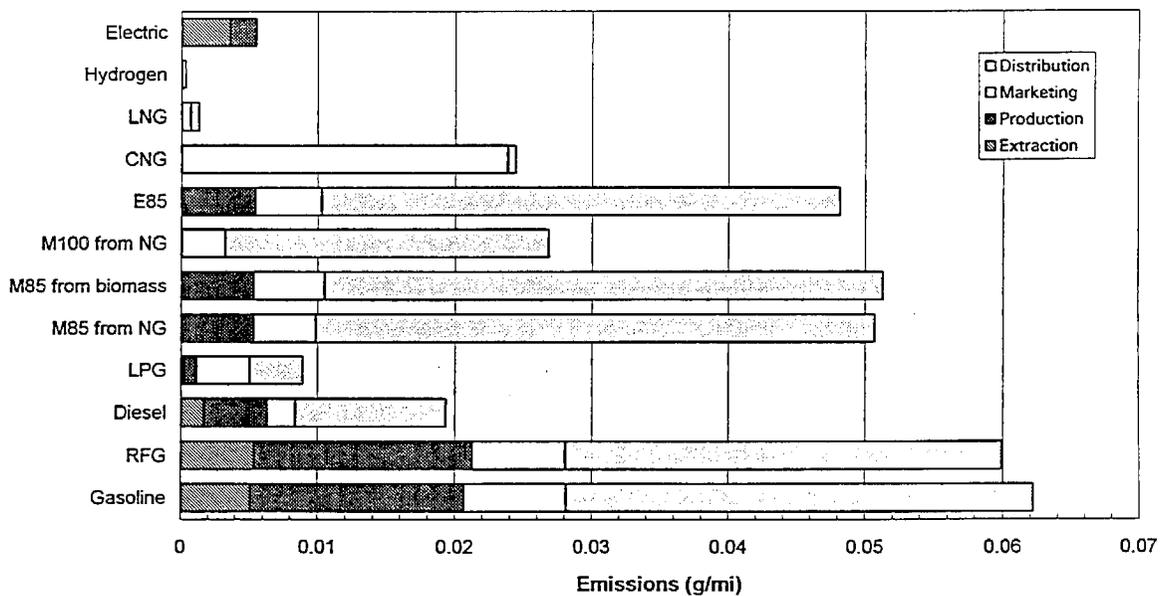


Figure S-4. Average NMOG, Scenario 2, South Coast (g/mi)

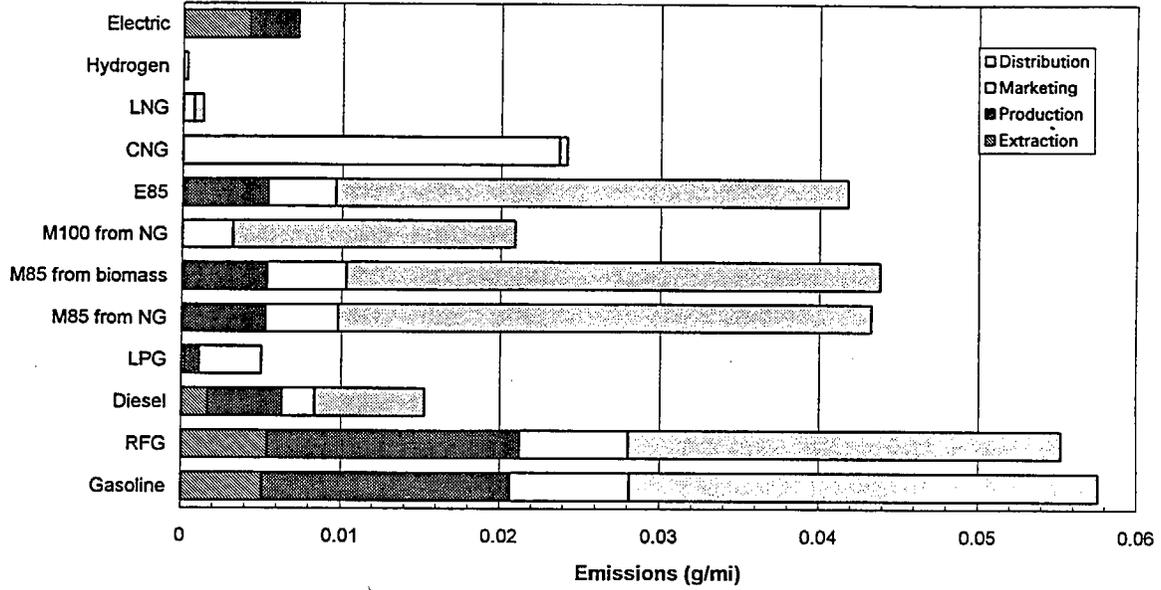


Figure S-5. Average NMOG, Scenario 3, South Coast (g/mi)

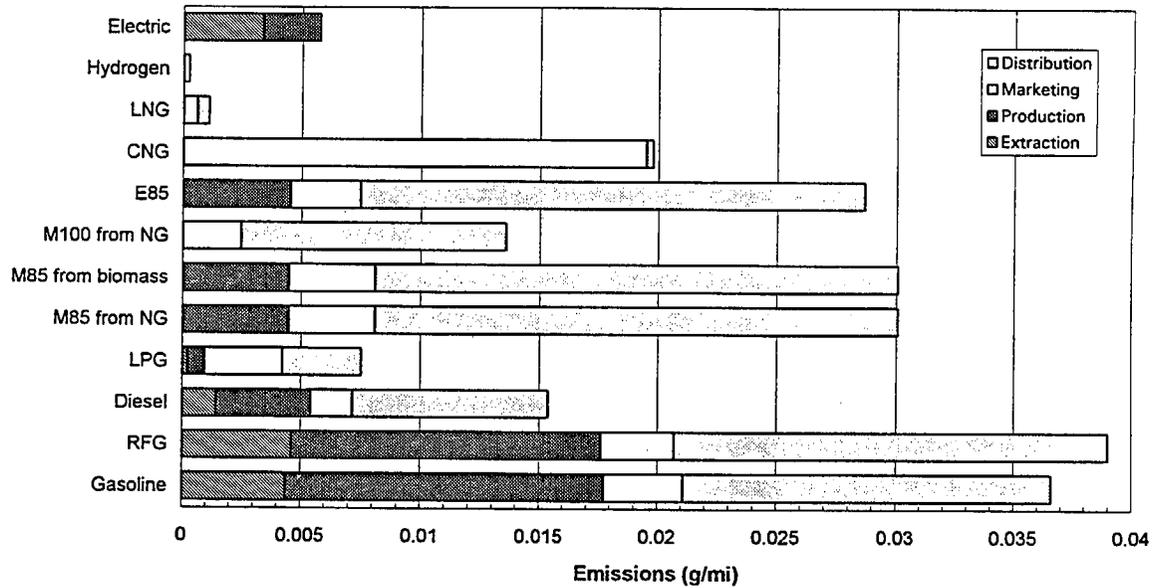


Figure S-6. Average NMOG, Scenario 4, South Coast (g/mi)

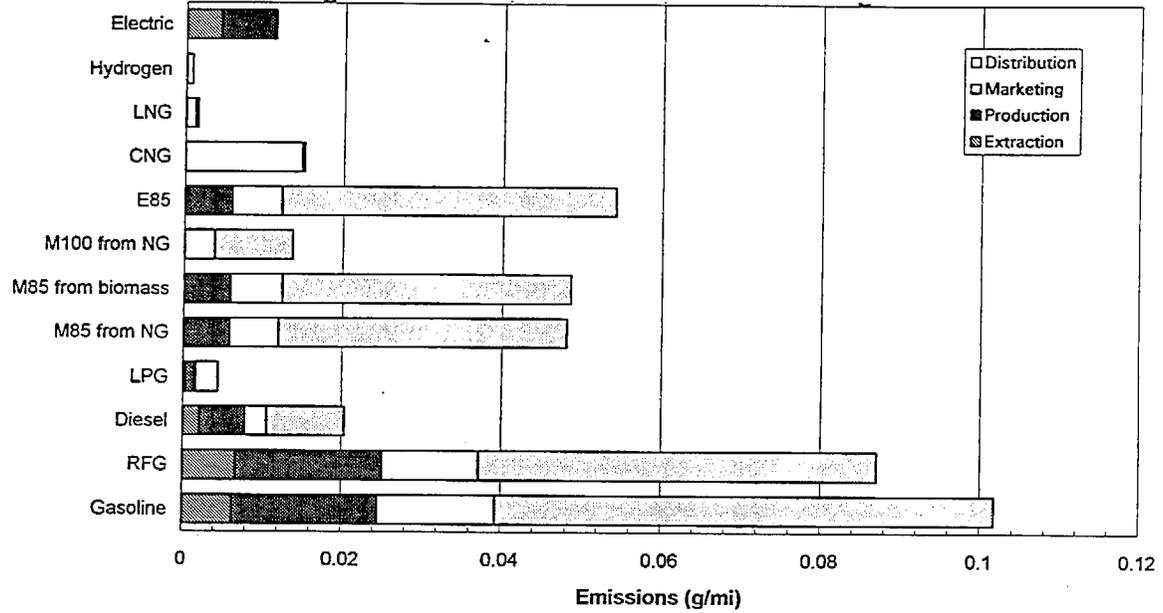


Figure S-7. Average ozone potential (MIR), Scenario 3, South Coast (g/mi)

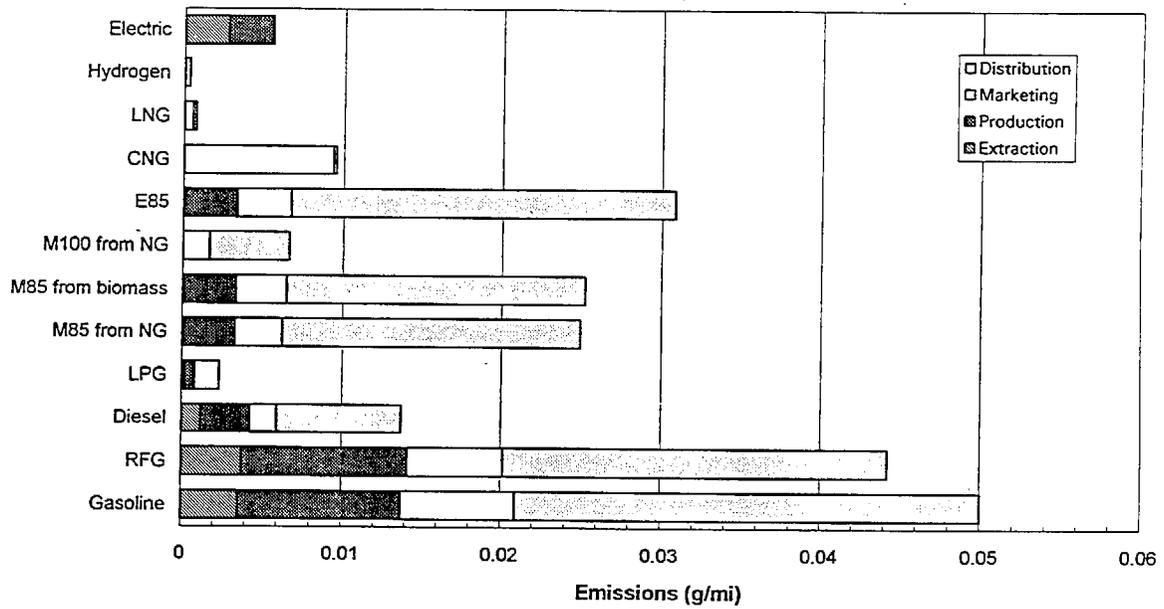


Figure S-8. Average ozone potential (MOR), Scenario 3, South Coast (g/mi)

On a global basis, gasoline and methanol from natural gas result in similar CO₂ emissions and substantial NO_x emissions from tanker ships. CO₂ emissions are lower for CNG, LNG, and electric vehicles, while biomass-derived fuels result in the lowest incremental CO₂ emissions.

The range in emission control assumptions and other parameters results in a significant range in fuel-cycle emissions. For example, the expected range in NMOG emissions is from 0.04 to 0.08 g/mi. Many of the assumptions for alternative-fuel use are the same as those for gasoline use. Thus, the ratio of alternative-fuel emissions to gasoline emissions for a given set of assumptions is less variable than the range in g/mi emissions.

S.2 MARGINAL FUEL-CYCLE EMISSIONS

Fuel-cycle emissions are also evaluated in the context of marginal emissions associated with a moderate increment of alternative fuel consumption or gasoline displacement. A moderately small use of alternative fuels would displace gasoline that would be imported into the South Coast Air Basin or allow for additional exports from the South Coast Air Basin, while a more aggressive alternative fuels penetration might lead to a reduction in refinery output. Small increments of alternative fuel use would displace emissions from fuel hauling, vehicle fueling, and possibly marine vessels used to import gasoline. On a small scale, other market conditions will influence refinery emissions more substantially than gasoline displacement due to alternative fuel use, leaving the refineries in the South Coast Air Basin operating at capacity. Many alternative fuels will be produced outside the South Coast Air Basin. Due to the location of alternative fuel production, as well as emission regulation considerations that apply to the South Coast Air Basin, marginal emissions correspond primarily to fuel trucking or distribution and local vehicle fueling. Marginal NO_x, NMOG, and ozone potential for Scenario 3 are shown in Figures S-9 through S-12.

ARB's zero-emission vehicle (ZEV) classification is based on zero emissions from vehicles. Comparing electric vehicle (EV) fuel-cycle emissions to those of other fuels indicates which other fuels might also be considered for ZEV status. Electricity for EVs used in the South Coast Air Basin will be generated there, in the rest of California, and outside of California. Marginal emissions from power generated in the South Coast Air Basin are limited by several factors. Non-utility power generators in the South Coast Air Basin will not contribute to new power generation, as their capacity is already incorporated into the current power generation mix and adding new non-utility capacity is not economically attractive. Furthermore, existing facilities in the South Coast Air Basin could not increase emissions beyond current permit levels, and new facilities would need to purchase offsets. Power plants in the South Coast Air Basin are subject to the Regional Clean Air Incentives Market (RECLAIM) regulation of the South Coast Air Quality Management District (SCAQMD), which provides a cap on power plant NO_x emissions for each utility. For larger usages of EVs in 2010, power generation will result in zero additional NO_x in the South Coast Air Basin due to RECLAIM limits. Marginal NMOG emissions from EVs do not include fugitive losses from natural gas pipelines.

Marginal emissions from reformulated gasoline distribution correspond to about 0.03 g/mi of hydrocarbons and 0.002 g/mi of NO_x from delivery trucks. The rate of alternative fuels penetration would affect marginal emissions from gasoline production. If the growth in gasoline exports exceeded or matched the gasoline displaced by alternative fuels, the impact on refinery NO_x and hydrocarbon emissions would be zero. If gasoline imports were rising to meet vehicle demand, alternative fuels would displace NO_x emissions corresponding to 0.01 g/mi from marine vessel

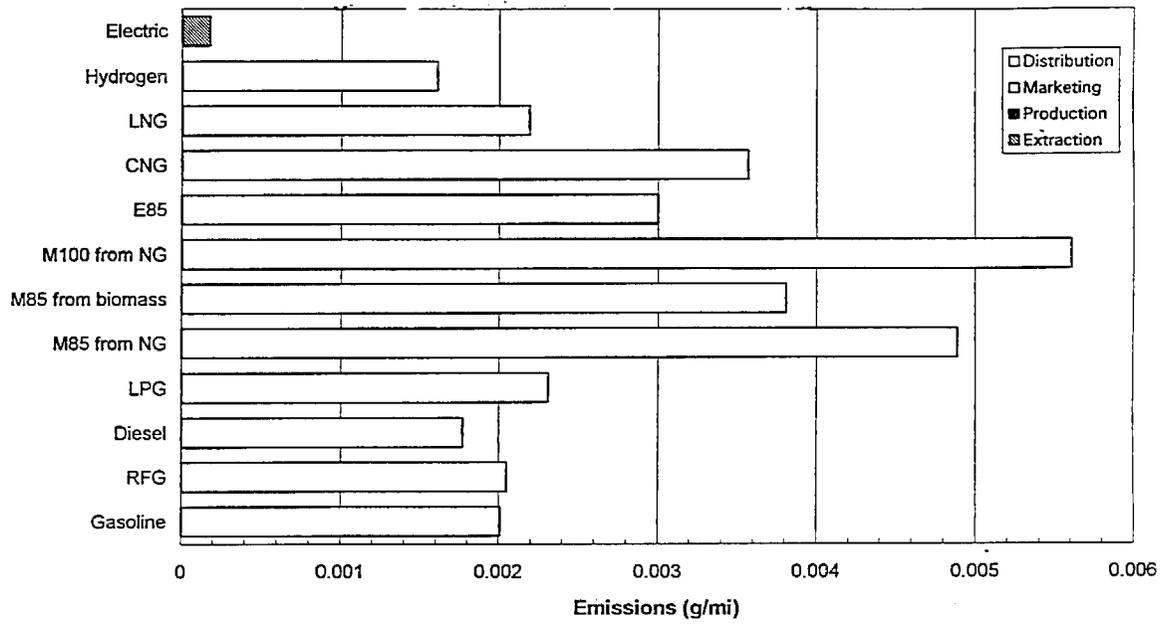


Figure S-9. Marginal NO_x, Scenario 3, South Coast (g/mi)

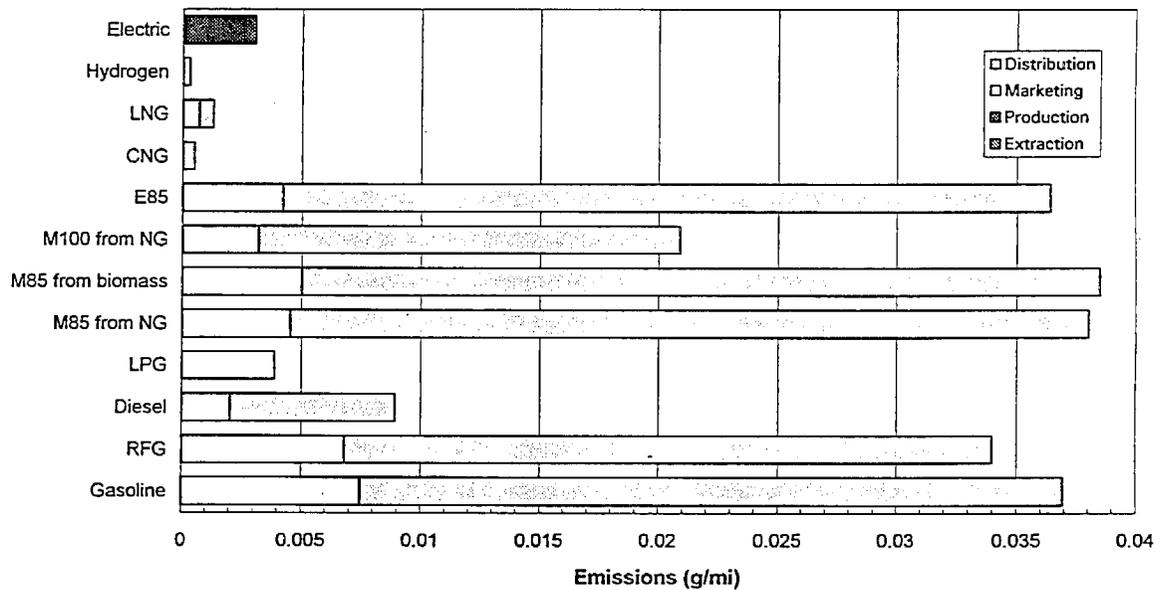


Figure S-10. Marginal NMOG, Scenario 3, South Coast (g/mi)

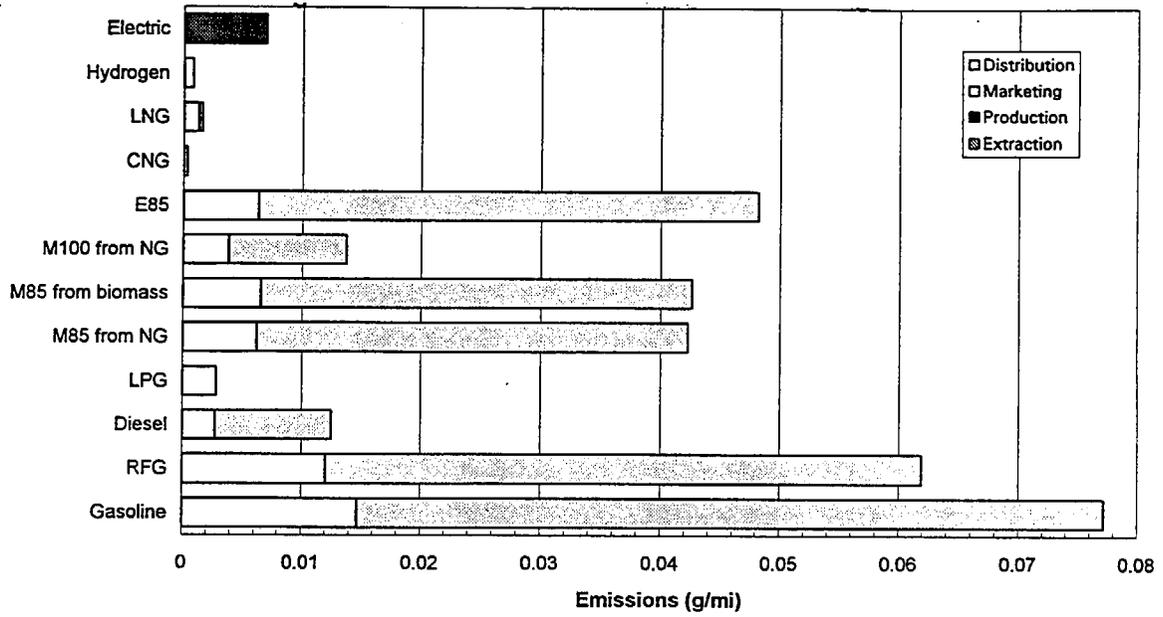


Figure S-11. Marginal ozone potential (MIR), Scenario 3, South Coast (g/mi)

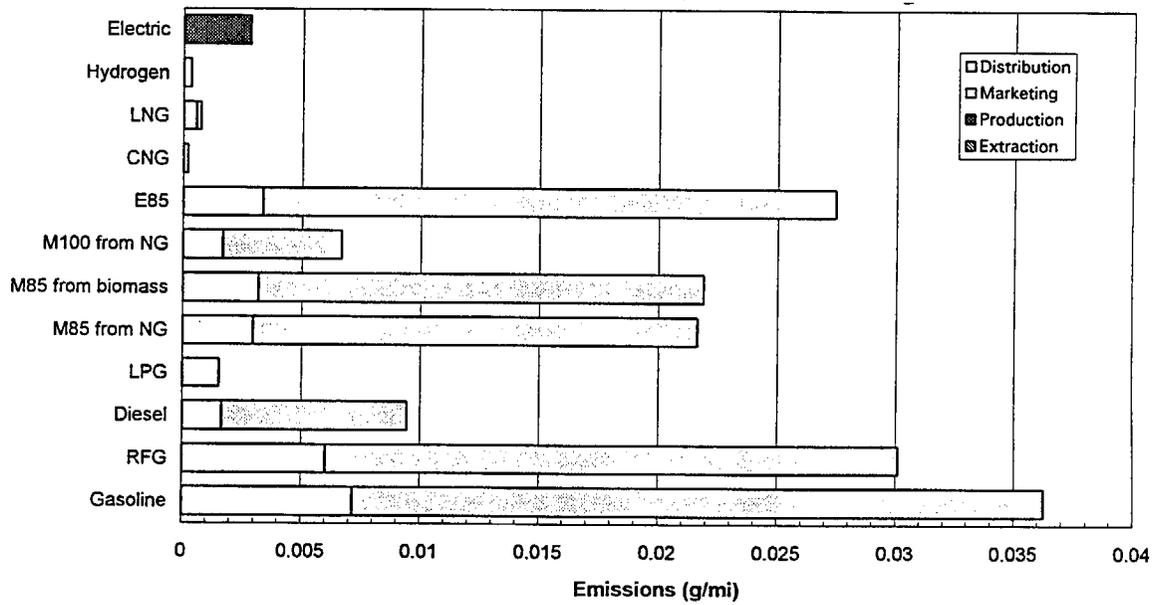


Figure S-12. Marginal ozone potential (MOR), Scenario 3, South Coast (g/mi)

operations in the South Coast Air Basin. Importing methanol by ship would result in more than 0.01 g/mi of NO_x from tanker ships due to the fuel's lower energy density. This source of NO_x would be avoided with ethanol, methanol, and hydrogen produced from biomass in California, as well as CNG and domestic LNG.

SECTION 1

INTRODUCTION

This study investigated the emissions associated with the production and distribution of conventional and alternative fuels. Emissions from the production and distribution of fuels are known as the fuel-cycle emissions and these can be significant in comparison to tailpipe emissions. Compared to currently available automotive fuels such as gasoline and diesel, alternative fuels have received attention because of their potential for reducing tailpipe exhaust emissions of criteria pollutants. Examining the fuel-cycle emissions of alternative-fueled vehicles appears relevant when assessing the overall environmental impact of these vehicles from both global and local perspectives. The California Air Resources Board's (ARB's) zero-emission vehicle (ZEV) classification is based on zero emissions from electric vehicles (EVs); therefore, fuel-cycle emissions associated with incremental electric power generation might be compared with incremental fuel-cycle emissions from conventional fuels. This study did not consider vehicle exhaust emissions (other than CO₂ which is proportional to fuel consumption) or vehicle evaporative emissions, since considering the variability in emissions and regulatory considerations was beyond the scope of this effort.

In California, the reactivity of exhaust emissions is considered in the certification of alternative-fueled automobiles. The ARB has developed ozone potential factors for individual reactive organic gas species (ARB, 1992, #92-59) found in vehicle exhaust. The ozone potential of vehicle exhaust is used to determine a reactivity adjustment factor (RAF) that is then multiplied by the numerical value of the non-methane organic gas (NMOG) exhaust mass emissions (in grams per mile [g/mi]) to determine compliance with the applicable NMOG standard. The ozone potential of evaporative emissions or fuel-cycle emissions is currently not considered in the certification of vehicles.

Understanding fuel-cycle emissions is one element in the overall emissions impact of alternative-fueled vehicles. Alternative-fueled vehicles have a potentially lower reactivity-adjusted fuel-cycle hydrocarbon emissions impact since these fuels consist of compounds with a relatively low ozone potential. Since a significant element of the total California fuel-cycle emissions inventory for gasoline vehicles appears to be fugitive emissions from the storage and distribution of fuels, one might expect fuels with a lower ozone potential to result in a net reduction in ozone potential. However, many factors including vehicle refueling frequency and fuel economy affect the relative emissions impact of different fuels. Fuel-cycle emissions also include emissions from fuel production facilities, bulk storage facilities, ships, pipelines, railroad tankers, and tanker trucks, as well as from retail storage and vehicle refueling facilities. An assessment of emissions is also complicated by the desire to compare marginal emissions which would result from the marginal use of new fuels. Ideally, one might project what production and storage equipment is displaced for a given amount of gasoline displacement. However, these infrastructure changes are also affected by economic conditions and market considerations. Changes in gasoline infrastructure will most likely not be linear with alternative fuel use but rather occur in step changes.

This study determined fuel-cycle emissions of NO_x, NMOG, methane, CO, and CO₂. Reactivity adjusted NMOG emissions are a principal focus of this study. The reactivity effect of NMOG emissions is represented as an ozone potential calculated from reactivity factors expressed as the maximum incremental reactivity (MIR) conditions or the maximum ozone reactivity (MOR) conditions.

The following sections discuss and review the methods used in this study to estimate and calculate the fuel-cycle emissions.

1.1 OBJECTIVE AND APPROACH

The objective of this study was to develop estimates of the fuel-cycle mass emissions on a per vehicle mile basis. The ozone potential of NMOG emissions was a particular focus of this study. The fuel-cycle emissions associated with production and distribution of conventional and reformulated gasoline (RFG), diesel, methanol and ethanol blended with RFG (M85, E85), liquefied petroleum gas (LPG), compressed natural gas (CNG), liquefied natural gas (LNG), hydrogen, and electricity were evaluated. One hundred percent methanol and ethanol (M100 and E100) were included in this study, as these are components of M85 and E85. M100 was also considered as a vehicle fuel.

The following outline summarizes the steps used in this study:

- Determine the physical characteristics and properties of all the fuels and feedstocks
- Evaluate the chemical compositions of the fuels, feedstocks, and their storage vapors as well as the products of combustion of fuel production equipment
- Outline scenarios for the production and distribution of fuels
- Determine the emissions of NO_x, CO, CO₂, CH₄, and NMOG for the processes involved with each scenario
- Determine the ozone potential per gram of NMOG emissions (specific reactivity) for different fuel-cycle emission streams
- Combine the specific reactivity of NMOG with per gallon fuel-cycle emissions
- Compare fuel-cycle emissions on a per mile basis

In this study, fuel-cycle emissions were first determined per unit of fuel, which allows for better comparison with other studies and provides better insight into the origin of the emission estimates. Afterwards, the emissions were related to fuel economy to determine g/mi emissions. This approach allows other values for fuel economy to be investigated more readily.

1.2 STUDY SCOPE AND ORGANIZATION

Table 1-1 summarizes the fuel/feedstock combinations that were considered in this study. As indicated in the table, several fuel/feedstock combinations are complicated by the fact that several products are made from the same feedstock and most fuels can be produced from several feedstocks.

Table 1-1. Fuels, feedstocks, and refining processes evaluated in this study

Feedstocks	Processes	Fuels
Crude Oil	Oil refinery operations	Conventional gasoline Reformulated gasoline Diesel LPG
Natural gas Coal Biomass Waste materials	Steam reforming Gasification	Methanol (M100) M85 (blended with reformulated gasoline)
Corn Sugar cane Biomass Waste material	Fermentation	Ethanol (E100) E85 (blended with reformulated gasoline)
Natural gas	Gas stripping and treatment	CNG LNG LPG
Natural gas Biomass Solar energy	Reforming Gasification Electrolysis	Hydrogen
Crude oil Natural gas Coal Biomass	Utility boilers Cogeneration facilities Non-fossil power	Electricity

Different mixes of feedstocks are also used in fuel production. A variety of crude oil sources make up the feedstock for California refineries and this mixture will change in the future. Methanol is currently produced from natural gas, while production from coal or biomass have been considered as options for the future. Similarly, biomass energy crops are envisioned to displace corn and sugarcane as feedstocks for ethanol. Non-fuel byproducts are also produced from oil refineries and ethanol plants. Natural gas is produced from gas fields as well as a byproduct of oil production and the gas can be used as either CNG or LNG fuels. LPG is produced during oil refining and derived from natural gas liquids, a product of natural gas production. Most LPG sold in California is produced in oil refineries. Both hydrogen and electricity can be produced from a myriad of feedstocks.

The alternative fuels listed in Table 1-1 are used to a limited extent in California. Many vehicles have been converted to operate on CNG and LPG and manufacturers are beginning to offer purpose-built vehicles. The natural gas industry worked on a strategy to sell several million natural gas vehicles in the U.S. within the next 20 years. Several thousand fuel-flexible methanol vehicles (FFVs) have been built as production vehicles for operation in California. FFVs are capable of

operating on either M85, gasoline, or any mixture of these fuels. These vehicles are also being produced for E85 operation. Pure forms of methanol or ethanol can also be used as vehicle fuels. However, M100 and E100 are usually considered more long range options for optimized dedicated vehicles. Except for hydrogen-powered fuel-cell vehicles, this study did not evaluate advanced vehicles with substantial increases in fuel efficiency. A variety of fuels could be used in fuel-cell-powered vehicles with on-board reformers. In addition, hybrid vehicles can also operate with increased fuel efficiency. EVs will make up a significant portion of California's vehicle fleet as part of ARB's Low-Emission Vehicle (LEV) program. Expanded use of EVs has also been considered as a means of reducing emissions to meet federal Clean Air Act emission requirements. The feedstocks in Table 1-1 may not all be used in the short term. The significance of feedstock options and combinations of fuels and feedstocks that are addressed in this study are discussed in Section 4.

Fuel-cycle emissions were analyzed over a range of assumptions. The major factors that affect fuel-cycle emissions in this study include the following:

- Differences in vehicle fuel economy (which are proportional to fuel-cycle emissions)
- Reduction in emissions due to stationary control measures in Southern California
- Different alternative-fuel production feedstocks and technologies

Emissions were estimated for conditions in the early 1990s and 2010 with emission regulations and vehicle fuel economy consistent with these time periods. Estimating emissions for the year 2000 was considered at one time; however, given the uncertainties in fuel economy, incremental emission considerations, and emission factors, such an estimation implies more precision to the overall emission estimates than is warranted. Early 1990s emissions and 2010 emissions serve as upper and lower bounds. Table 1-2 shows the scenarios explored in this study.

Table 1-2. Scenarios and timing for fuel production and distribution

Scenario	Year	Description
1	1992	Current emissions. Equipment meets prevailing standards. Refinery emissions based on 1990 SCAQMD inventory. Current on-road vehicle fuel economy.
2	2010	Equipment meets standards applicable in year 2010. Refinery emissions adjusted from 1990 inventory for local rules. Emissions consistent with ARB factors for fuel distribution. Currently available fuel production and distribution processes. Improved fuel economy.
3	2010	Same as Scenario 2. Lower assumptions on distribution emissions. New alternative fuel production facilities and technologies. Lower fuel spillage.
4	2010	Same as Scenario 3. Lower energy input assumptions for alternative fuel processing. Improved gasoline vehicle fuel economy and further efficiency improvements for alternative-fueled vehicles.

A significant fraction of the new vehicle mix in the year 2010 is expected to be comprised of ultra-low-emission vehicles (ULEVs). This time period is appropriate for the evaluation of fuel-cycle emissions since a significant fraction of ULEVs may be alternative-fueled. For ULEVs (and other LEVs), compliance with the applicable NMOG emission standard is determined by multiplying the exhaust NMOG mass emissions for a vehicle by the RAF assigned to that vehicle type. Hence, an alternative-fueled vehicle could emit higher or lower emissions than the applicable NMOG standard, provided that the impact on ozone formation is equal to a vehicle which meets the standards while operating on conventional gasoline. Therefore, an examination of reactivity adjusted fuel-cycle emissions is relevant.

Assumptions were made regarding which technologies represent current and future fuel production. Scenario 1 represents the current situation (early 1990s) and Scenarios 2, 3, and 4 represent a range of emission estimates for the year 2010. The assumptions for each scenario correspond to parameters discussed in Section 4. With the exception of EVs and hydrogen-powered vehicles in Scenarios 2, 3, and 4, this study is based on conventional internal-combustion-engine-powered vehicles with the focus on examining differences in ozone potential for similar vehicles. High-fuel-efficiency technologies such as hybrid vehicles were not considered. Advanced vehicle fueling systems that minimize refueling emissions were also not considered except for gaseous fuels where reductions in venting will be required by law.

Fuel-cycle emissions are calculated first in g/unit fuel which allows for the evaluation of other fuel economy assumptions. Vehicle fuel economy affects total fuel demand which could also affect fuel-cycle emissions. Total fuel demand would affect the throughput through fueling stations as well as the interpretation of where the marginal increment of fuel is produced. However, these effects are minor in relation to the direct effect of fuel economy on total fuel-cycle emissions.

Figure 1-1 shows the general fuel-cycle steps associated with fuel production and distribution. These steps are categorized into eight production and distribution phases shown in Table 1-3. These phases are grouped into the categories extraction, production, marketing, and distribution which are later used for presenting the results of the study in Section 6.

This study followed the approach used by other studies (Unnasch, 1989; DeLuchi, 1991; and Brandberg, 1992). Emissions are estimated for steps in the fuel production and distribution process. This study relied on both process-specific analyses, using emission factors for fuel-cycle steps, as well as emission inventories or aggregate data. This report is organized along the modular approach that was used to calculate emissions.

Other than combustion and fugitive emissions associated with fuel production and distribution and vehicle CO₂ emissions, no other environmental impact were considered in this study. In order to consider the total emissions from fuel production and distribution, exhaust and evaporative emissions need to be added to the fuel-cycle emissions in this study. Only emissions from fuel production equipment were considered in this study. Emissions associated with the production of equipment, facilities, or vehicles have not been included in this report. Spills and upsets were only considered when they were part of routine operations. For example, the probability weighted emissions from fuel tanker shipment spills were not considered, but average emissions from vehicle fueling spills were counted.

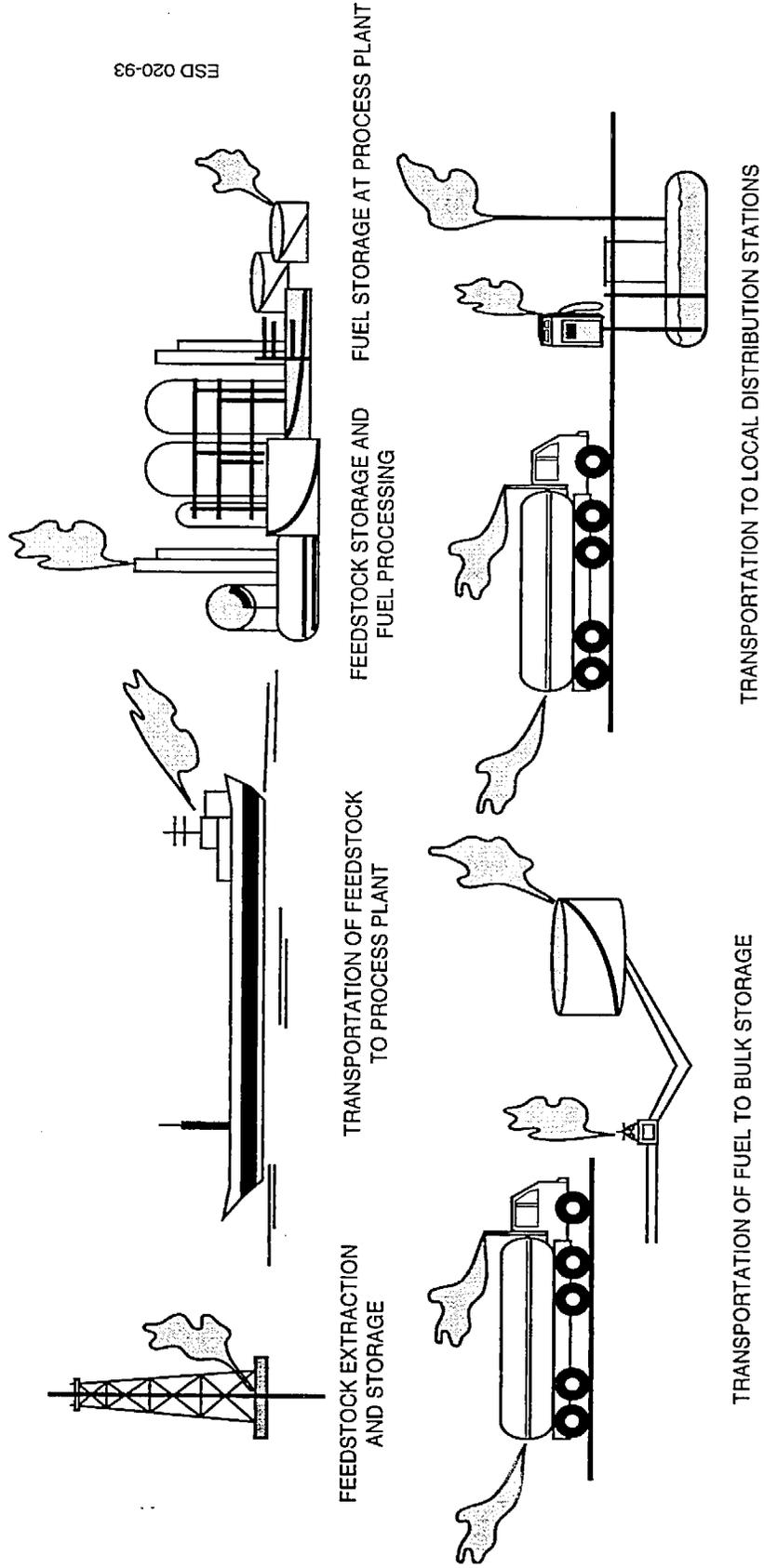


Figure 1-1. Fuel-cycle steps and associated emissions sources

Table 1-3. Fuel-cycle emissions were categorized into eight production and distribution scenarios

Phase No.	Description
<u>Extraction</u>	
1.	Feedstock extraction
2.	Feedstock transportation
<u>Production</u>	
3.	Fuel processing/refining
<u>Marketing</u>	
4.	Fuel storage at processing site
5.	Transport to bulk storage
6.	Bulk storage
7.	Transport to local distribution station
<u>Distribution</u>	
8.	Local station distribution

Section 2 of this report outlines the basic assumptions regarding fuel compositions and fuel properties used in the study. Important fuel properties that affect the analysis included the following:

- Fuel composition — Determines speciated composition and subsequent properties
- Vapor pressure — Determines vapor concentration in storage tank head space and related vapor emissions
- Vapor molecular weight — Used to determine mass of vapor concentrations in storage tank head space
- Higher heating value — Used to determine fuel consumption rates for various processes
- Lower heating value — Used to compare vehicle fuel consumption

Section 3 discusses NMOG speciation data for fuel, fuel vapor, and exhaust emissions. Ozone potential factors are used to determine the specific reactivity for various emissions sources. Section 4 presents an overview of the fuel production scenarios for each fuel. The geographical area where fuels are produced and distributed are identified in order to account for transportation and distribution emissions. Emission rates for equipment that are used in the production and distribution of fuels are presented in Section 5. A data base approach was used to relate the mix of equipment, storage, and transportation modes in Section 4 with emission rates in Section 5. Ozone potential values for speciated emission profiles in Section 3 are also related to emission rates in Section 5. The results

per unit of fuel produced are presented in Section 6. A final series of calculations relates vehicle fuel economy with emissions per unit of fuel to show the fuel-cycle emissions on a g/mi basis.

1.3 PROJECT MEETINGS

Several review meetings were held during the course of this study. Attendees at these meetings included representatives from the following organizations. Many of the industry attendees expressed reservations about this study; these reservations are discussed later in the report. We appreciate the constructive comments that were received on the study, and these are discussed in the report.

- California Air Resources Board
- California Energy Commission
- South Coast Air Quality Management District
- Western States Petroleum Association
- California Natural Gas Vehicle Coalition
- Western Liquid Gas Association
- California Electric Transportation Coalition
- Southern California Gas Company

The following parties were invited to attend project review meetings and provide input for this study, but decided not to participate in meetings:

- Sacramento Metropolitan Air Quality Management District
- Parallel Products
- American Methanol Institute

Other interested parties that received copies of the report for review include the following:

- Argonne National Laboratory
- Pacific Northwest Laboratory
- National Renewable Energy Laboratory
- Oak Ridge National Laboratory

1.4 ACKNOWLEDGEMENTS

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The study was completed with the assistance of the following subcontractors:

- MARTECH International
- Basic Research
- Invictus Corporation
- Robert Penny Enterprises
- J.T. Nowell and Co.

SECTION 2

FUEL AND FEEDSTOCK PROPERTIES AND COMPOSITIONS

The fuels and feedstocks studied have different properties and compositions that affect their fuel-cycle emissions. This report accounts for the effect of fuel composition on processing requirements and efficiency, evaporative and fugitive emissions, and combustion emissions. These fuel and feedstock properties and compositions are summarized in this section. The relevant properties include vapor pressure, liquid density, vapor molecular weight, carbon content, and heating value. Each fuel and feedstock is discussed in the following sections. Table 2-1 summarizes the energy and carbon content of the various fuels discussed throughout this report (Phillips, Schmidt). A range of properties corresponds to most of the fuels and feedstocks in Table 2-1. The values in the table are representative of average compositions. Methanol, ethanol, MTBE, hydrogen, CH₄, and CO are pure compounds with invariant compositions. Feedstocks such as coal, crude oil, and biomass have a wide range in carbon content and heating value. For coal and crude oil, the range in the ratio of carbon content to energy content (or lb CO₂/MMBtu) is relatively small (Schmidt, Guthrie).

Carbon content as weight percent or per MMBtu is used to determine CO₂ emissions from fuel combustion. Higher heating values are used to relate fuel use to energy consumption for process efficiency calculations while lower heating values are used to compare vehicle fuel consumption. The molecular weight of fuels corresponds to vapor density and associated evaporative emissions. The values in Table 2-1 were used throughout the report.

Energy content of fuels is affected by the hydrogen, carbon, and oxygen content. Oxygenated fuels contain less energy per unit mass than conventional hydrocarbons since the hydrogen and carbon in the fuel is already partially reacted with oxygen. Non-oxygenated hydrocarbon fuels that have a high hydrogen to carbon ratio generally have higher energy contents in Btu/lb and a lower energy content in Btu/gal. Figure 2-1 shows the trend in higher heating values as a function of carbon content for various fuels and feedstocks. Non-oxygenated hydrocarbons, hydrogen, and carbon form a continuous curve while oxygenated compounds have reduced heating values and lie below the hydrocarbon curve. Figure 2-2 shows the volumetric energy content of fuels over a closer range of hydrogen to carbon ratio. The reduced energy content and increased volumetric fuel consumption of alcohol and liquefied gaseous fuels is well known. Reformulated gasoline also has a reduced volumetric energy content compared to conventional gasoline. The reduction in energy content is due to the addition of oxygenates as well as the addition of more hydrogenated components which have lower volumetric energy contents.

2.1 FUEL COMPOSITION AND PROPERTIES

Fuel composition and properties affect many aspects of the fuel-cycle analysis. Liquid fuel and vapor composition and properties are necessary to predict emissions from fuel transfer operations. The vapor pressure of fuels affects the mass emissions from vapor transfers. The composition of

Table 2-1. Energy and carbon content of fuels

Fuel ^a	Carbon Content		Energy Content				Density (lb/gal)
	C (wt %)	HHV ^b (lb CO ₂ /MMBtu)	HHV (Btu/lb)	HHV (Btu/gal)	LHV ^c (Btu/lb)	LHV (Btu/gal)	
Conventional gasoline	84.6	149	20,800	124,600	19,200	115,400	6.0
Reformulated gasoline	82.8	149	20,300	122,000	18,800	113,000	6.0
Low Sulfur diesel	86.7	159	20,010	139,680	18,300	130,800	7.2
Low aromatics diesel	85.9	161	19,560	137,990	18,750	129,350	6.9
Methanol	37.5	141	9,800	64,800	8,600	57,000	6.6
Ethanol	52.1	149 (0) ^d	12,800	84,400	11,600	76,200	6.6
M85 (85% methanol)	44.0	142	11,375	75,200	10,000	65,400	6.5
M85 (87% methanol)	43.4	143	11,090	72,350	9,855	64,392	6.5
E85 (85% ethanol)	56.3	148 (22) ^d	13,925	91,300	12,600	81,700	6.5
E85 (83% ethanol, 1.8% butane)	56.7	149 (22) ^d	13,955	90,354	12,707	81,870	6.5
CNG ^e	73.6	120	22,500	103,000 ^f	20,300	92,800 ^f	4.6 ^f
Residual oil	90.0	181	18,300	148,200	17,700	143,800	8.1
Crude oil	84.5	162	19,100	147,800	—	—	7.7
Coal	66.6	202	12,100	—	—	—	—
LNG	74.0	117	23,100	80,900	20,800	72,900	3.5
LPG from petroleum	82.0	139	21,570	90,600	19,770	83,200	4.2
Hydrogen	0.0	0	61,100	32,400 ^f	51,600	27,400 ^f	0.53 ^f
Liquid hydrogen	0.0	0	61,100	35,700	51,600	30,100	0.58
MTBE ^g	68.1	153	16,300	100,900	15,100	93,500	6.2
CH ₄	75.0	115	23,900	101,200 ^f	21,500	91,100 ^f	4.2 ^f
CO	42.9	362	4,300	32,400 ^f	4,346	32,400 ^f	7.5 ^f
Carbon	100	260.3	14,087	215,000	14,087	215,000	15.3

^aM85 and E85 values were calculated based on blending with reformulated gasoline. Different M85 and E85 blends are shown, since these fuels can be blended with varying alcohol constituents.

^bHHV = Higher heating value.

^cLHV = Lower heating value.

^dBiomass-based carbon is not counted in fuel cycle CO₂ emissions.

^eNatural gas distributed in California.

^fPer 100 scf.

^gMTBE = Methyl tertiary butyl ether (CH₃OC₄H₉).

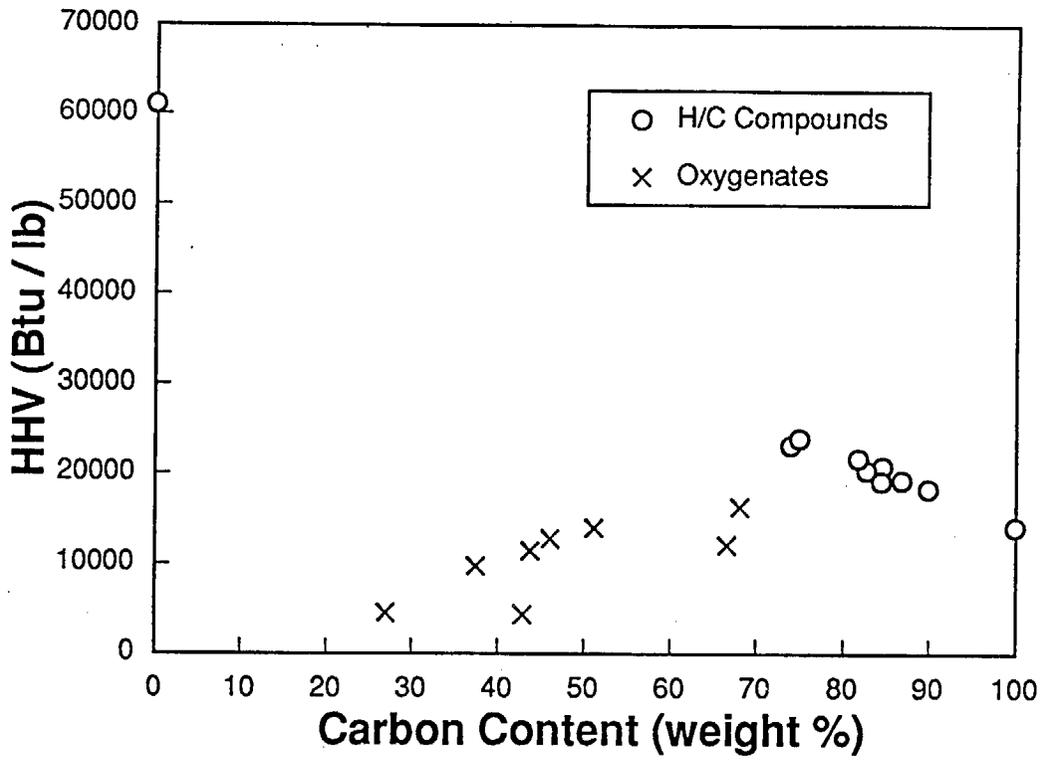


Figure 2-1. Higher heating value versus carbon content for energy carriers (Btu/lb)

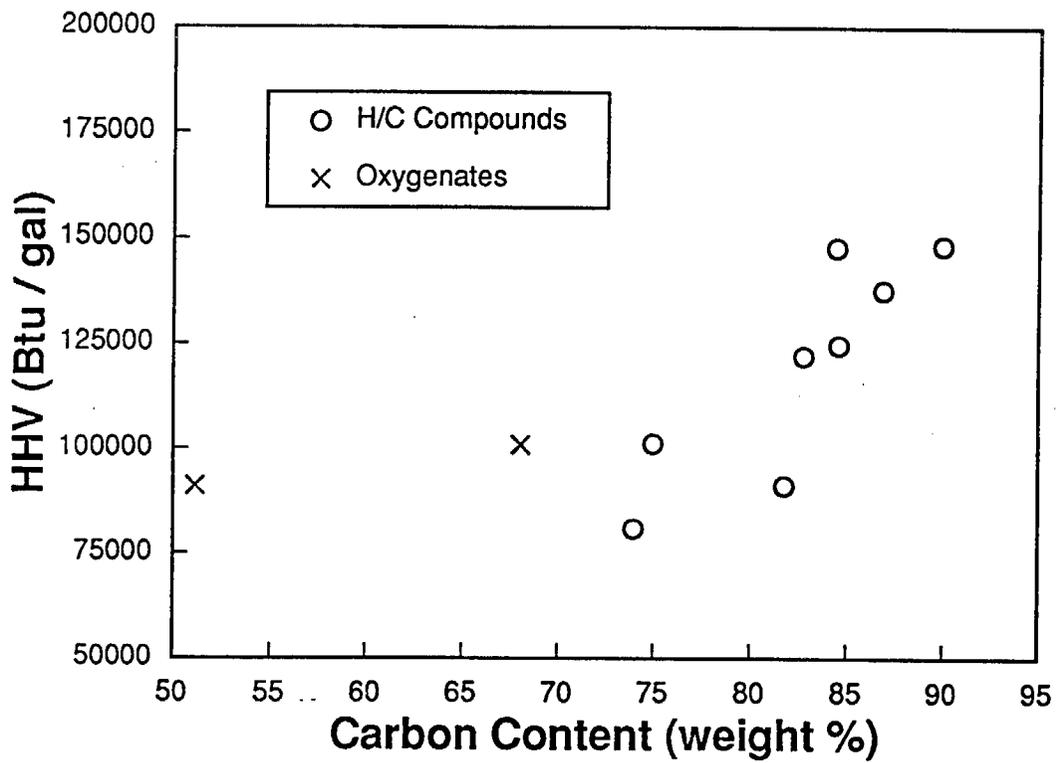


Figure 2-2. Higher heating value versus carbon content for liquid fuels (Btu/gal)

fuels affects the ozone potential of liquid spills as well as that of vapor emissions. Gasoline specifications affect refinery energy requirements and emissions. Finally, the composition of blended fuels needs to be consistent with values used for energy content, vapor pressure, and vehicle fuel economy.

A considerable number of data are available on gasoline compositions and physical properties as well as exhaust and evaporative emissions from gasoline- and alternative-fueled vehicles. The following sections summarize the physical properties of the fuels considered in this study. Since the fuels in this study can be represented by a variety of formulations, presenting the potential range in fuel properties provides some insight into how the results of this study might be affected by different fuel properties. The purpose of Sections 2.2 through 2.5 is to identify which liquid fuel formulations were used for speciation analyses in the context of the range of possible formulations.

Data on vapor compositions in fuel tanks are limited. Furthermore, polar compounds like alcohol exhibit non-linear vapor pressure behavior when blended with hydrocarbons. Two approaches were used to assess vapor compositions. ARB's Engineering Testing Section collected liquid and fuel vapor samples and analyzed these for composition and physical properties. Liquid and vapor compositions of these fuels and alcohol blends were determined for a variety of fuel storage conditions. The compositions of RFG, M85, and E85 blends were provided to Mobil Research and Development Company so that the vapor compositions could be determined from a vapor space model under identical temperature conditions. The composition of the vapor space is addressed in Section 2.7, "Liquid Fuel Vapor Composition."

2.2 CONVENTIONAL GASOLINE

Gasoline is by far the most widely used automotive fuel in California. A conventional gasoline available in 1989 was used as the baseline fuel against which reformulated gasoline and alternative fuels would be compared. Gasoline varies seasonally and among producers. As the ambient temperature falls during the winter, gasolines with high RVPs (Reid Vapor Pressure, >10 psi) provide better cold starting. With the higher ambient temperatures of summer, gasolines with low RVPs (<10 psi) reduce vapor emission losses. The properties of gasoline are important in determining the evaporative emissions from many fuel-cycle steps. Table 2-2 summarizes the fuel properties of various gasolines and seasonal blends, such as winter and summer blend gasolines. Several fuel formulations are presented to show the range in properties and to verify that the fuel properties assumed in this study are within reasonable limits.

The baseline conventional gasoline used in this study should represent summer gasoline that was available in 1989. A major objective of the study is to evaluate emissions on a reactivity basis by comparing their ozone potential. Since ozone is chiefly a concern during summer months, gasolines that meet summer time vapor pressure limitations are the focus of this study. The seasonal definitions of summer and winter vary regionally and are documented by ARB (ARB, 1991).

Considerable data on gasoline properties and compositions have been published. Examining the range of fuel properties provides insight into the validity of fuel properties that were used in this study. ARB compiled data on gasoline properties for summer and winter formulations. An ozone modeling study (Harley, 1992) presented a composite gasoline that represented 1987 summer gasoline with similar vapor pressure and composition by hydrocarbon class. This reference provided both vapor and liquid compositions for a fuel that closely represents California gasoline. Furey also

Table 2-2. Properties of conventional gasoline

Gasoline/Reference	Type	RVP ^a (psi)	API ^b Gravity	Octane No. ^c	Distil. Temp. (°F)			Sulfur (ppm wt)	Benzene (vol %)	Olefin (vol %)	Aromatics (vol %)	Oxygen (wt %)	MTBE ^d (vol %)	Profile No.
					10%	50%	90%							
Several requirements for gasoline (ASTM-D 439) ^e	A	9.0			158	250	374							—
	B	10.0			149	245	374							—
	C	11.5			140	240	365							—
	D	13.5			131	235	365							—
	E	15.0			122	230	365							—
California state averages (ARB., 1991) ^f	Average	9.2			125	212	329	151	1.71	9.60	32.26			—
	Winter	11.1			115	206	324	146	1.78	9.84	30.17			—
Composite 1987 (Harley, 1992)	Summer	8.4			129	215	331	153	1.68	9.51	33.07			—
	CA	8.5			—	—	—	—	1.98	9.8 ^g	36.3 ^g	0	0	—
Arco regular unleaded (Boekhaus, Feb. 1991)	RUL	8.8	54.6	87.2	122	223	347	—	1.8 ^g	12.3 ^g	33.6 ^g	0.06	0.3	9011
	PUL	8.9	55.0	92.8	131	233	329	125	1.9	6.8	41.5	0	0	9009
Arco premium unleaded (Boekhaus, Feb. 1991)	RF-A	8.72	57.4	87.3	128	218	330	339	1.53	9.2	32.0	0	0	9005
	RF-C	8.74	50.2	94.0	136	213	288	284	1.33	3.3	43.8	2.78	15.4	9006
Industry estimate table (Boekhaus, 1991)	Average	8.6	—	—	—	213	323	349	1.6	9.7	34.4	0	—	—
	RUL	10.8	—	—	—	—	—	—	1.52 ^g	2.82 ^g	29.37 ^g	0	0	9003
Indolene (Furey, 1986)	Test fuel	8.9	—	—	—	—	—	—	2.90 ^g	1.04 ^g	39.38 ^g	0	0	9001
Industry average (ARB, 1994)	RF-A	8.65	—	—	124	214	333	—	1.48	9.2	31.4	0.02	0	9996

^aRVP = Reid vapor pressure.

^bAPI = American Petroleum Institute. API Gravity = 141.5/(Specific Gravity @ 60°F)-131.5.

^cOctane No.: (RON+MON)/2.

^dMTBE = Methyl tertiary butyl ether.

^eAll limits represent maximums.

^fJanuary through June volume weighted averages.

^gData presented in percent by weight. For aromatics including benzene multiple by 0.84 to estimate vol %.

presented vapor and liquid compositions for Indolene test fuel and a gasoline formulation with higher vapor pressure. A wealth of data is available on an industry average fuel, identified as RF-A in the Auto/Oil study. This fuel is not entirely representative of California gasoline. Its vapor pressure is 0.3 psi higher than that of average California summer gasoline shown in Table 2-2 and the sulfur content of RF-A is about twice that of California gasoline. However, the octane number as well as benzene, olefin, and aromatics content of RF-A is quite close to California averages published by ARB. ARB uses RF-A as a fuel for baseline comparisons. The oil industry considers other fuel formulations more representative of California gasoline. For the purposes of this study, the composition of RF-A was used to evaluate ozone potential. For evaporative emission estimates it was assumed that the fuel has an RVP of 8.4 psi. Actual vapor composition data from RF-A will be used to evaluate reactivity in Section 3. The higher sulfur content of RF-A would affect exhaust mass emissions and have less of an impact on the composition and reactivity of the liquid fuel since the RVP, olefin, and aromatics content of RF-A are close to those of California summer gasoline. Speciation modeling and vapor composition analysis were based on the RF-A fuel blended for ARB (ARB, 1994).

Other gasoline compositions have also been published. ARCO published a variety of gasoline speciations and fuel properties including those for premium gasoline and several other reformulations (Boekhaus, 1991). Premium gasolines typically have higher aromatic contents which is reflected in ARCO PUL and a high octane fuel from the Auto/Oil program (RF-C). Indolene does not come close to representing commercial gasolines because of its low olefin content and high benzene content. Low olefin content helps storage stability. Gasolines with compositional speciations are indicated by a profile number in Table 2-2. The ozone potential of these fuels is discussed in Section 3.

2.3 REFORMULATED GASOLINE

Phase 2 reformulated gasoline will be used in 1996. Gasoline reformulation can improve emissions through the following mechanisms:

- Reduced vapor pressure lowers evaporative emissions
- Reduced light olefins lower the reactivity of the lighter hydrocarbons in the evaporative emissions
- Reduced heavy aromatics lower the reactivity of unburned exhaust emissions
- Oxygenates contribute to lower CO emissions and have a low ozone potential
- Reduced benzene in gasoline reduces benzene emissions and toxics risk
- Reduced sulfur levels result in lower mass emissions from vehicle exhaust

Several of these strategies will be incorporated into reformulated gasolines. All Phase 2 gasolines are expected to have lower concentrations of sulfur and benzene and higher concentrations of oxygenates. ARCO has developed reformulated gasoline for older cars (EC-1) and EC-X for current cars (Boekhaus). Phase 2 gasoline certification fuel is currently available from Phillips Petroleum. ARB uses this test fuel for vehicle emission testing. Several batches of Phase 2 fuel have been tested and are presented in Table 2-3. EC-X also meets Phase 2 specifications, but a speciated

Table 2-3. Properties of reformulated gasoline

Gasoline/Reference	Type	RVP ^a (psi)	API ^b gravity	Octane No. ^c	Distil. Temp. (°F)			Sulfur (ppm wt)	Benzene (vol %)	Olefin (vol %)	Aromatics (vol %)	Oxygen (wt %)	MTBE ^d (vol %)	Profile No.
					10%	50%	90%							
Phase 2 (ARB, 1991)	Phase 2 limit	7.0 ^e	—	>87	—	220	330	80	1.2	10.0	30.0	1.8 to 2.7 ^f	—	—
Average Phase 2 ARB projection	Phase 2	7.0	—	—	—	200	290	30	—	4.0	22	1.8 to 2.2	—	—
EC-X (Boekhaus, 1991)	EC-X	6.7	—	—	—	201	293	41	0.8	5.5	21.6	2.7	14.9	—
EC-1 (Boekhaus, Feb. 1991)	EC-1	7.6	60.4	88.0	128	209	351	245	1.0	10.0	19.0	1.0	5.5	9012
EC-P (Boekhaus, Feb. 1991)	EC-P	8.1	57.6	92	132	202	320	113	1.0	12.5	23.6	2.3	12.5 ^g	9010
Phillips certification fuel (Phillips)	Phase 2	6.8	60.3	92.4	133	200	292	38	1.1	5.8	26.2	1.96	10.8	—
Phase 2 (Auto Oil, 1994)	Phase 2 (C2)	6.8	—	—	—	209	293	31	0.93	4.1	25.4	2.0	11.2	—
Phillips certification fuel (ARB, 1994)	Phase 2	6.6	—	—	140	209	297	—	0.83	4.48	24.0	2.0	11.1	9796

^aRVP = Reid vapor pressure.

^bAPI = American Petroleum Institute. API Gravity = 141.5/(Specific Gravity @ 60°F)-131.5.

^cOctane No.: (RON+MON)/2.

^dMTBE = Methyl tertiary butyl ether.

^eApplicable during summertime control periods only.

^fApplicable during wintertime control periods only.

^gwt %.

profile was unavailable. EC-X has a lower aromatics content and a higher MTBE content than the Phase 2 certification fuel. EX-P is a high octane fuel but unlike unrefined premium gasolines, it contains less than 25 percent aromatics. Hydrocarbon compositions are available for these fuels in Appendix A. Ozone potential values used in this study were determined from speciation modeling and vapor composition analysis that were based on Phase 2 fuel blended for ARB (ARB, 1994).

Phase 2 gasoline specifications include a 1.8 to 2.2 wt percent oxygen requirement which can be met with compounds such as MTBE, ETBE, or TAME (tertiary amyl methyl ether). A 2-percent oxygen fuel content is equivalent to the addition of 11 percent MTBE which is the basis for Phase 2 gasoline in this study. Cap values were established to provide a set of specifications for enforcement and do not necessarily represent the average set of specifications which would be encountered in the market. For enforcement, the cap values are necessary to establish a uniform set of specifications which all gasoline will be required to meet.

Fuel producers can take one of two approaches to comply with the provisions of the Phase 2 gasoline regulations. A fuel producer could elect to simply follow ARB's specifications. A fuel producer could also certify an alternative formulation based on exhaust emission data from vehicle testing or certify an alternative formulation based on predictive models. ARB expects that most Phase 2 gasolines will meet the adopted specifications. Based on considerations for meeting Phase 2 specifications, ARB staff indicated that an RVP of 7.0 would better represent average Phase 2 gasoline values (Venturini, 1993). Oil industry sources indicated that the RVP of reformulated gasoline would be under 6.8 psi.

Historically, the RVP of conventional gasoline has been about 0.5 psi below the limit. As the RVP limit is lowered, the actual RVP of reformulated gasoline may not be as low as 0.5 psi below the limit. The RVP for Phase 2 gasoline used in this study is 6.8 psi to represent an RVP for summertime gasoline that falls within the compliance limits. This value lies between those recommended by oil industry comments and ARB staff. Table 2-4 shows the properties of conventional and Phase 2 gasoline and diesel that were used in this report.

Table 2-4. Properties of gasoline and diesel used in this report

Fuel	RVP^a (psi)	LHV^b (Btu/gal)	Oxygen (wt %)	MTBE^c (wt %)	Sulfur (ppm wt)
1989 conventional gasoline	8.4	115,400	0	0	150
Phase 2 gasoline	6.8	113,000	2	11	40
Diesel	0.03	130,800	0	0	200

^aRVP = Reid vapor pressure.

^bLHV = Lower heating value.

^cMTBE = Methyl tertiary butyl ether.

^dSummer blend gasoline.

2.4 DIESEL

Diesel fuel is used to fuel compression-ignited light-and heavy-duty engines. The popularity of diesel as a fuel for passenger cars has dropped in recent years while diesel is the dominant fuel for trucks. Unlike gasoline, diesel has a low vapor pressure and a low octane number. High quality diesel is characterized by a high cetane number. The ARB implemented a specification for clean diesel that took place in October 1993. This fuel required lower sulfur and aromatics (0.05 and 10 percent maximum, respectively) with an option to meet an alternative specification that results in equal emission benefits. This study assumes the use of reformulated diesel meeting the alternative specification throughout. ARB expects that most complying diesel fuel will be produced to meet alternative formulations rather than the 10 percent aromatics specification. Two Chevron alternative formulations have sulfur contents of 54 and ppmw and 196 ppmw. These fuels had average cetane values of 58 and 59 while the ASTM specification is a cetane number of 40. ARB expects sulfur content to be less than 200 ppmw and average aromatics content to be between 18 and 24 volume percent. The properties of diesel fuel for this study are shown in Table 2-4. RVP values for diesel are not frequently measured. EPA's document on emission factors from stationary sources (AP-42) shows true vapor pressures for diesel fuel as a function of fuel temperature. The low aromatics alternative formulation has a slightly reduced volumetric heating value compared to that of alternative diesel formulations. The heating value for the more prominent alternative formulation is assumed in this study.

2.5 M85 AND E85

The chemical compositions of E85 and M85 fuel formulations in this study are based on blending with Phase 2 reformulated gasoline. This scenario is likely, given that the expected demand for alcohol fuels will not prompt the oil industry to develop special gasolines for M85 blending. The RVP of alcohol/gasoline blends does not behave with a linear relationship. Some information on the RVP of oxygenate gasoline blends can be found in the literature. Alcohols, which are polar compounds, form azeotropes with non-polar gasoline components. This effect results in a higher vapor pressure than would be predicted through a linear relationship such as Raoult's law. As shown in Figure 2-3, the increase in vapor pressure is most prevalent for low level alcohol blends.

After an initial peak in RVP is formed at approximately 5 percent methanol, the RVP drops with increasing methanol content. At the M85 level, the RVP is slightly lower than that of the 9 psi blend gasoline. Commingled M85/gasoline blends that are mixed in the fuel tank of an FFV, will result in a higher vapor pressure for fuel in the tank. Data from Furey combined with the Phase 2 gasoline RVP can be used to estimate the RVP of M85 (Figure 2-3). If methanol were blended with reformulated gasoline with an RVP of 6.8 psi, the relationship in Figure 2-3 would predict the M85 blend to have an RVP of 7.5 psi. Measurements of M85 blended with Phase 2 certification fuel were performed by ARB and as part of the Auto/Oil study (Auto/Oil, August 1994). The resulting M85 blend had RVPs of 7.1 and 7.2. Table 2-5 shows the vapor pressure and distillation data for gasoline blends tested by ARB and the Auto/Oil program. Both the M85 and the E85 fuels were blended to conform to ARB's RVP specifications. The methanol content of the M85 blend was 86.8 percent by volume which serves to suppress the vapor pressure.

Figure 2-3 also shows the vapor pressure of Indolene blended with various oxygenated compounds. All of the alcohols exhibit a non-linear RVP effect versus gasoline concentration. The resultant vapor pressure follows consistent trends in proportion to the RVP of the pure alcohol

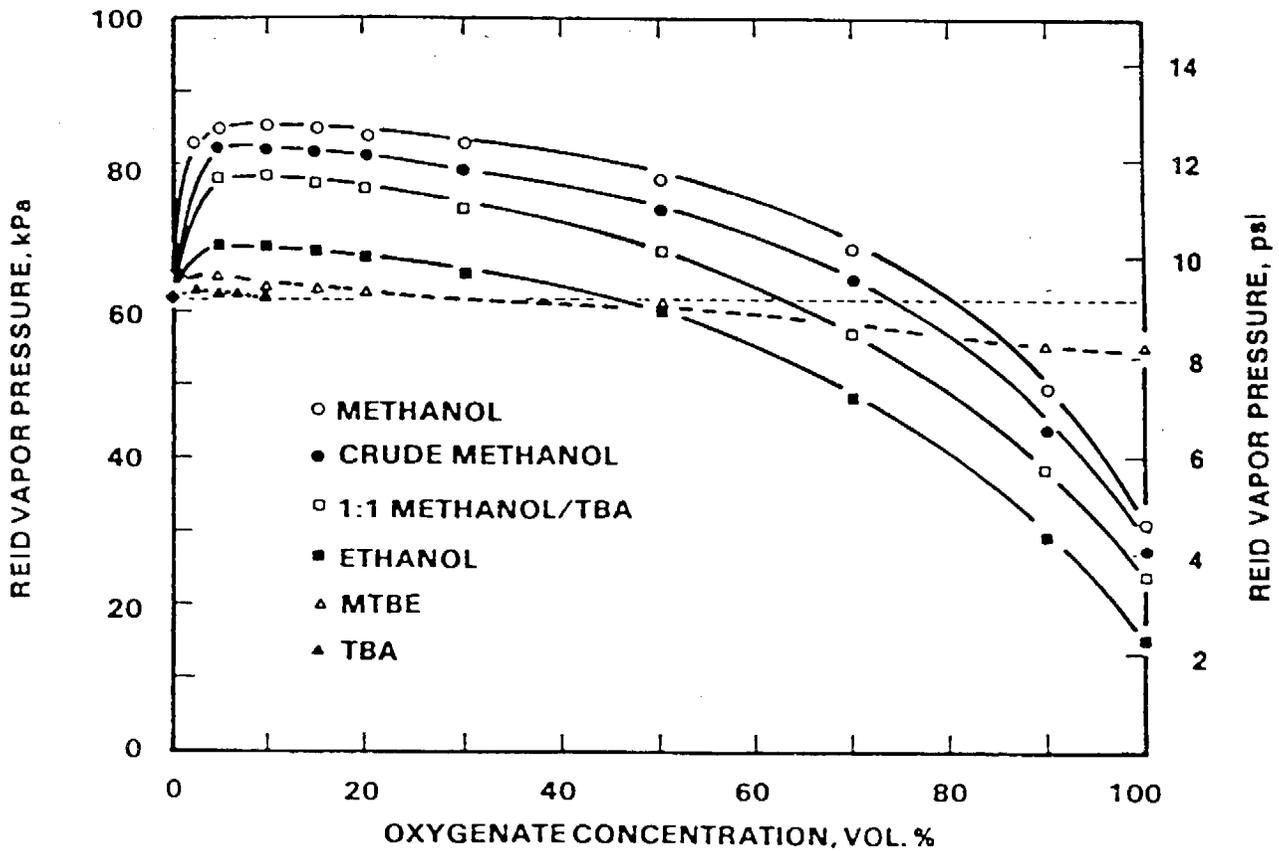


Figure 2-3. RVP of alcohol and MTBE blends in Indolene (Furey, 1985)

Table 2-5. Physical properties of gasoline and alcohol fuels

Fuel ^a /Lab-ID	RVP (psi)	Distillation (°F)				
		IBP	10%	50%	90%	End Pt.
Phase 2/ARB-lot 316	6.60	100	140	209	297	394
RF-A/ARB-lot 424	8.65	90	124	214	333	418
M85 (86.8% methanol/Phase 2)/ ARB lot 880	7.20	123	143	147	148	152
E85 (83.3% ethanol, 14.3 % Phase 2, 2.4% butane)/ARB	7.75	110	160	171	172	175
M85 (84.4% methanol, Phase 2)/ Auto/Oil ZC2	7.1	—	—	—	147	—
Phase 2/Auto/Oil C2	6.8	—	—	—	293	—

^aCompositions for M85 and E85 are shown in volume percent.

component. Extrapolating these trends to blend gasoline with an RVP of 6.8 would indicate an RVP of E85 of about 4.5. The RVP of E85 tested by ARB was increased by minimizing the ethanol content and adding butane to the fuel to achieve a resultant vapor pressure in the mid-range of ARB's specification. The RVP adjusted compositions were the basis for this study. These compositions determine the fuel speciation, vapor density, ozone potential, and heating value. The compositions also reflect the mix of fuel cycle emissions associated with fuel production. The 87 percent methanol and 83 percent ethanol mixtures shown in Table 2-5 are referred to as M85 and E85 in this report.

2.6 M100 AND E100

The composition of M100 and E100 are assumed to be 100 percent methanol and ethanol respectively. The properties of these fuels are shown in Table 2-1. The composition of fuel vapors is the same as that of the liquid. M100 and E100 can contain trace contaminants of water and hydrocarbons as allowed in ARB's specifications. Measurements of M100 contaminants from vehicle demonstration programs indicate negligible hydrocarbons and typically less than 1000 ppm water. The effect of this level of water on vapor pressure and heating value is negligible.

2.7 LIQUID FUEL VAPOR COMPOSITION

In July 1994, ARB collected liquid fuel and head space fuel vapor samples from two gasoline formulations, Phase 2 certification fuel, and RF-A¹, as well as from M85 and E85. The fuels were blended to meet emission certification specifications. The gasoline blending component for the alcohol mixtures was Phase 2 gasoline. In order to meet the RVP requirements of the fuel specification, the M85 and E85 fuels were blended with the mixtures indicated in Table 2-5. These samples were taken from a 55-gallon fuel drum and a vehicle fuel tank. The measurements were taken at various fill levels for the drum and fuel tank tests. Methanol and ethanol vapor samples were collected using impingers. Liquid and vapor speciation was performed by gas chromatography at ARB's Monitoring and Laboratory Division. ARB's Q.C. Special Testing Section analyzed liquid fuels for RVP, distillation curve, and specific gravity.

ARB's 1991 VW FFV was used for testing. To measure liquid fuel and head space vapor temperatures and head space pressure, a new OEM fuel tank was equipped with thermocouples and pressure sensors. A fuel drain was installed at the low point of the tank to ensure complete fuel draining. All measurements from the vehicle were taken with the OEM fuel cap in place. Precautions were taken to remove previous fuel from the vehicle fuel tank. Vapor samples were collected with vehicle fuel tanks at 100, 80, 40, and 10 percent full. The vehicle was driven 25 miles and parked for 2 minutes prior to collecting a vapor sample. The tests were performed in July and August 1994 with ambient temperatures ranging from 69 to 90°F. Each vehicle sampling routine was started in the morning and the vehicle was exposed to similar temperature conditions during vapor sampling. The results of this testing are incorporated into the following discussions of fuel properties and the analysis of NMOG speciation in Section 3. Additional measurements were performed in August 1995. The objective of this testing was to further evaluate the ozone potential of fuel vapors and are discussed in Section 3. The speciated data and sampling conditions are provided in Appendix A.

¹ All four fuels were blended by Phillips Petroleum Company. RF-A is a reference fuel for the Auto/Oil study.

California standards for E85 and M85 fuels place further constraints on the fuel formulation and resulting vapor pressure. M85 fuel specifications originally called for the same RVP limit as the prevailing gasoline. Vapor pressure constraints in the specifications no longer prevent splash blending. Therefore, the 7.2 RVP M85 blend that resulted from mixing M100 and Phase 2 gasoline would meet prevailing RVP requirements. M85 that is blended from Phase 2 gasoline will have different flame luminosity characteristics than other M85 blends because the gasoline component will contain fewer aromatics. Aromatics affect peak flame luminosity towards the end of the burn period while other gasoline components contribute more to luminosity during the start of the burn period. The fuel will also contain less butane than other M85 formulations. The reduced butane will affect the luminosity at the beginning of the burn. Reduced butane in Phase 2 gasoline will also make M85 and gasoline spills more difficult to ignite.

Specifications for E85 require a minimum RVP of 6.5 psi which can not be achieved through splash blending. Splash blended E85 would also have too low of an RVP for optimum cold starting in currently available FFVs. Another alternative for blending E85 would be to add butane to the fuel in order to achieve a final RVP of 6.5 psi. If a gasoline blending stock were specially prepared for E85 production, this gasoline could not be sold elsewhere in California since it would have too high an RVP. Splash blending butane at a bulk terminal would be hazardous because of butane's high volatility. RVP adjusted E85 could be produced at the refinery where there should be ample supplies of butane and blending could be accomplished under controlled conditions. Blending with pentane and isocrackate might result in better fuel weathering properties than blending with butane alone.

This study examined volatility adjusted E85. The resulting RVP of the blended E85 tested by ARB was the highest of all of the three fuels blended from Phase 2 gasoline. The butane content and RVP of this fuel is higher than required for cold starting. For volatility adjusted E85, it was assumed that a target RVP of 6.8 was achieved with the addition of butane. Table 2-6 shows the properties of alcohol fuels used in the study. Vapor pressures are used to determine evaporative emissions in Section 5 and lower heating values determine the fuel consumption for vehicles.

Figure 2-4 shows the compositions for the liquid fuels considered in this study except for diesel. The compositions, based on ARB's measurements, are presented as mass fractions. The liquid gasoline analyses contained about 8 percent unidentified components which is typical for these types of tests. The unidentified fraction is due to uncertainties in interpreting gas chromatograph peaks for heavier components. While not specifically identified, these components are a mix of heavy aromatics and paraffins. The differences between Phase 2 gasoline and RF-A are illustrated by the breakdown of liquid components. RF-A contains more aromatics and olefins which are replaced by MTBE in Phase 2 gasoline. Phase 2 gasoline was used to blend E85 and M85. The alcohol content of E85 is on the low end of the specification while M85 contains a higher alcohol fraction. The alcohol mass fractions of the E85 and M85 samples were 85 and 88 percent respectively. The mix of hydrocarbon components in Phase 2 gasoline is reflected in the alcohol blends. However, the E85 blend contains additional butane to achieve a vapor pressure that meets the 6.5 psi minimum. The vapor pressure of these fuels is shown in Figure 2-5. The vapor pressure of M85 could be higher if a higher RVP blending component were used or if the fuel was blended to a lower methanol content. Fuel suppliers may choose to target specific blends to optimize profits for market conditions and to maintain a margin of safety for vapor pressure constraints. The E85 fuel may have been blended too conservatively in the allowable vapor pressure range. This fuel had the highest vapor pressure of all of the Phase 2 gasoline blend even though the specification allows for a lower vapor pressure.

Table 2-6. Properties of alcohol fuels

Fuel ^a	RVP ^b (psi)	Component	Composition (vol %)	LHV ^c (Btu/gal)
M100	4.63	Methanol	100	57,000
E100	2.31	Ethanol	100	76,200
M85 ^d	7.2 ^e	Methanol	86.8	64,390 ^f
		Phase 2 gasoline	13.2	
E85 ^d	6.8 ^g	Ethanol	83.3	81,870 ^f
		Phase 2 gasoline	14.9	
		Butane	1.8	

^aM100 = 100 percent (neat) methanol, E100 = 100 percent (neat) ethanol, M85 and E85 are blended to meet ARB specifications including RVP constraints.

^bRVP = Reid vapor pressure.

^cLHV = Lower heating value.

^dAlcohol/gasoline fuel mixtures are based on Phase 2 gasoline properties. The composition of M85 corresponds to the methanol content necessary to meet ARB's "M85" specification. This mixture results in 87 volume percent methanol and is referred to as M85 throughout this study.

^eRVP for M85 is based on measurements of fuel blended for ARB.

^fBased on blending with Phase 2 gasoline, LHV of 113,000 Btu/gal, 11 percent MTBE.

^gRVP for E85 is assumed to correspond to the low end of the ARB specification. The vapor pressure is increased by adding 1.8 percent butane.

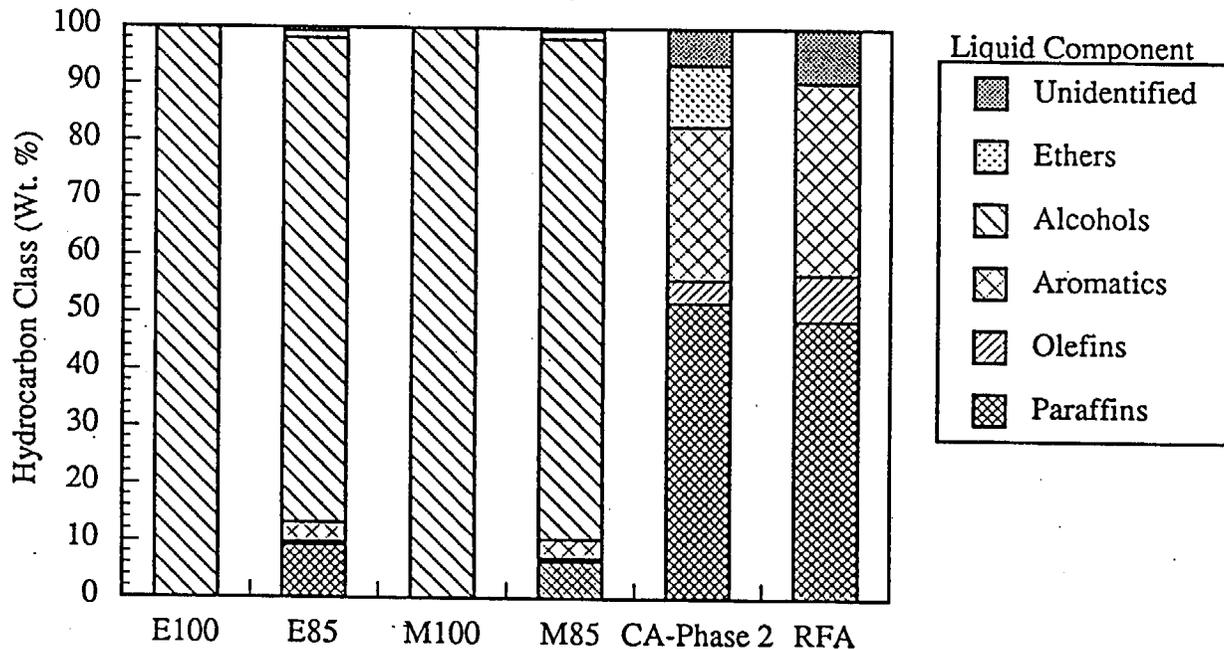


Figure 2-4. Liquid fuel composition

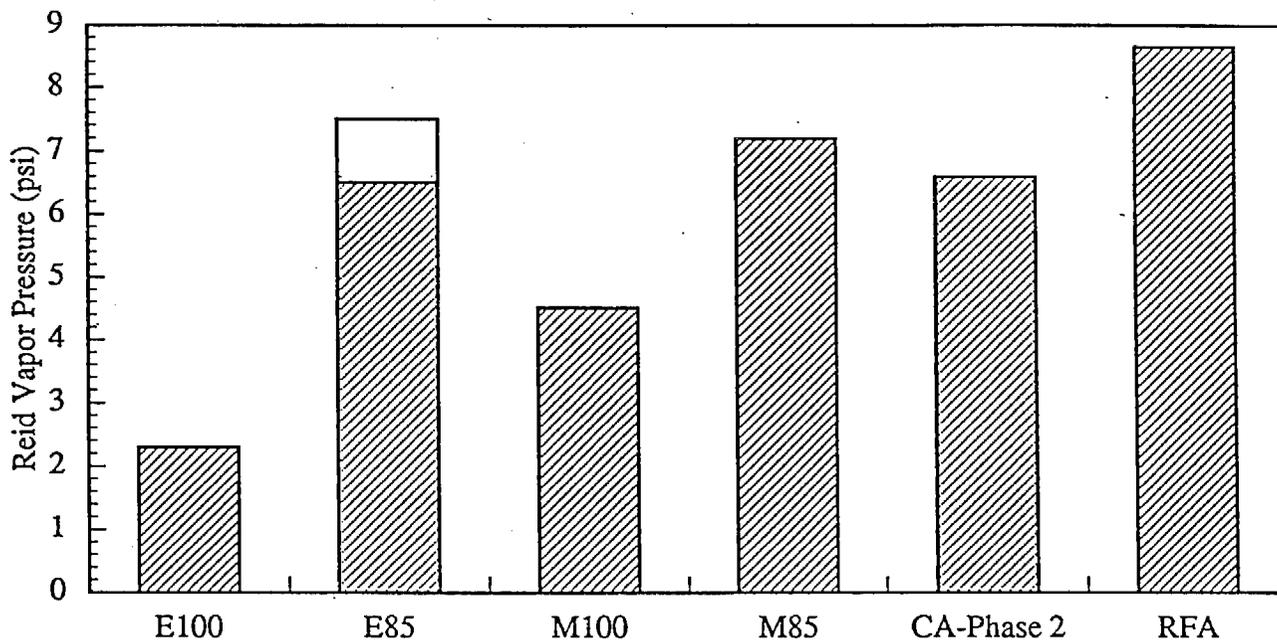


Figure 2-5. Reid Vapor Pressure of liquid fuels

Figure 2-6 shows the molecular weight of the liquid fuels. Phase 2 gasoline has a higher average molecular weight because light components such as butane are removed. The average molecular weight of the liquid fuels provide some insight into the vapor pressure behavior of the fuels. Ethanol is a heavier alcohol compared to methanol and consequently has a lower vapor pressure. The slightly higher molecular weight of Phase 2 gasoline reflects the absence of butane.

The vapor speciation tests provided data on vapor composition and hydrocarbon concentration. These tests were performed over real world test conditions and consequently, the vehicle and fuel drum tests were performed over a range of ambient temperatures. Vapor concentrations were determined with a flame ionization detector in order to establish the range for GC measurements. Subsequently, GC measurements of the vapor concentrations were performed. The vapor mass was calculated from the concentration data. The GC data were in agreement with FID measurements of vapor concentration.

Since these data are from uncontrolled real world tests, the influence of fuel temperature and weathering on vapor mass and composition needs to be considered. Figures 2-7 and 2-8 show the vapor mass as it varied with average liquid fuel and vapor temperatures as well as with the tank fill level. Both vehicle test data and drum data are shown. In some cases, the liquid and vapor were at similar temperatures while in others, primarily fuel drums, the vapor temperature was over 25°F higher than the liquid. Since the fuel vapor pressure increases with temperature, one would expect the vapor mass to increase with temperature. This is the general trend, with some notable excursions from the trend. All of the data make sense when viewed in the context of the liquid and vapor temperature as well as the fuel tank levels. A significant excursion from the temperature trend occurred with the RFA fuel drum. Two test points were near 69°F liquid temperature but the vapor mass concentration differed by 30 percent. Inspection of the temperature conditions shows that one

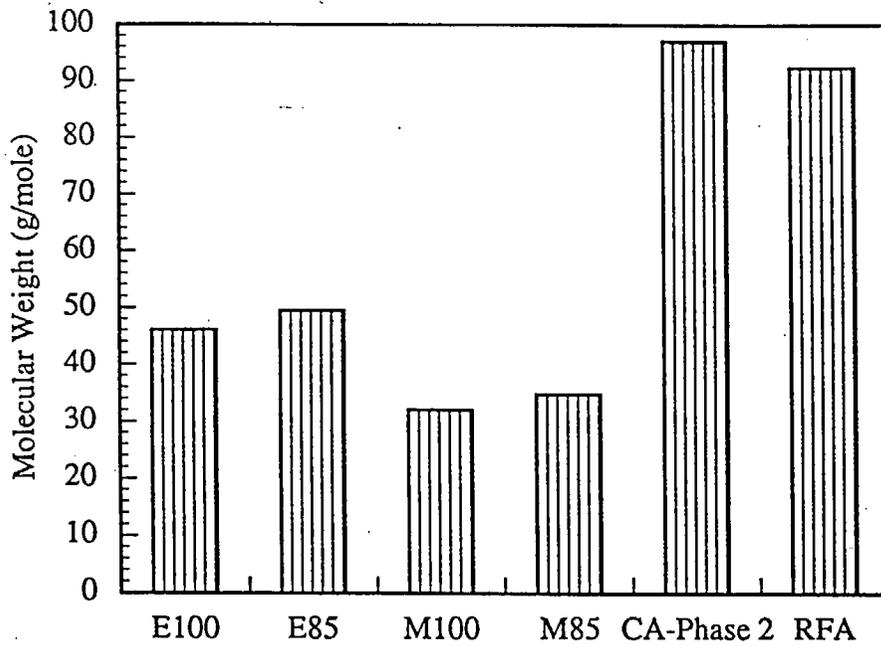


Figure 2-6. Average molecular weight of liquid fuels

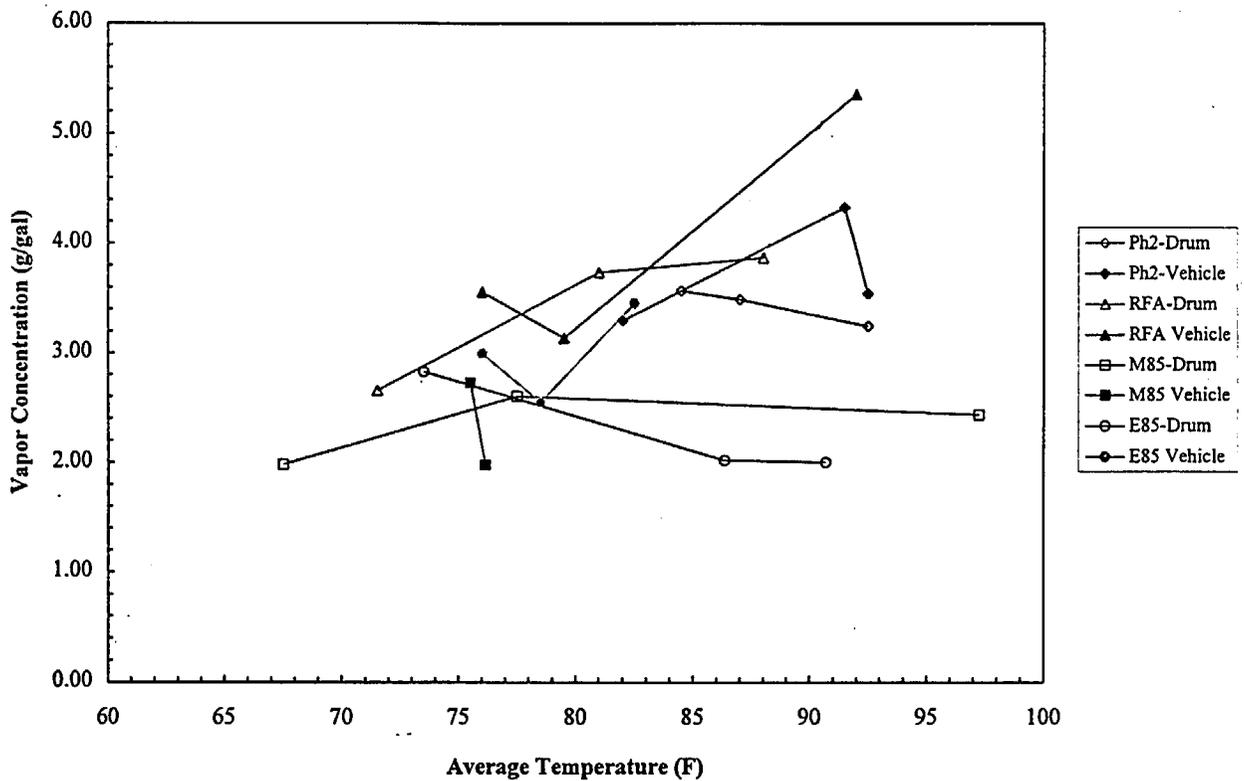


Figure 2-7. Vapor concentration versus average temperature

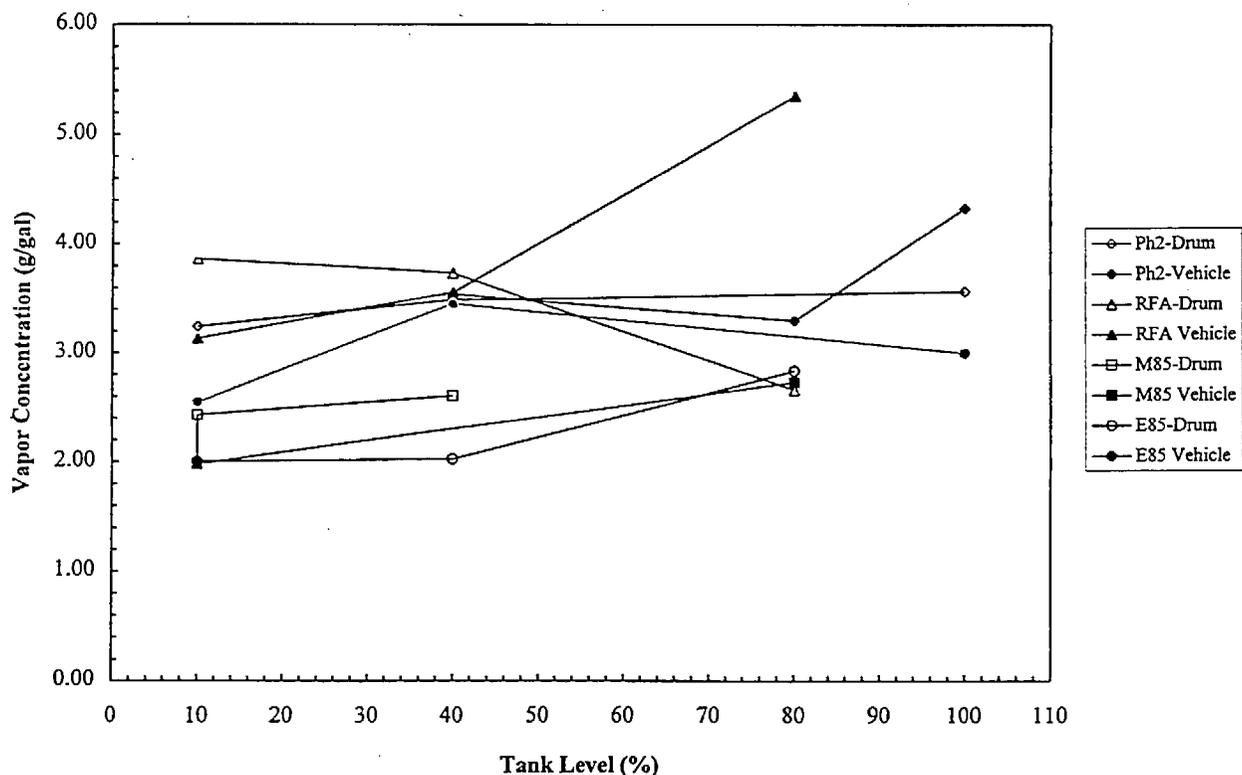


Figure 2-8. Vapor concentration versus tank fill level

test point occurred later in the morning after the drum had warmed up the vapor temperature significantly, but the liquid temperature had not changed. The E85 mass concentrations are lower at higher temperatures. This effect is due to weathering of the fuel. The fuel level, vapor pressures and vapor concentrations are summarized in Section 3.

The tests with RFA in relatively cool drums is an accurate representation of underground storage tank conditions where the temperature is close to 70°F and stable. Actual underground storage tank vapors contain the vapor that is recovered from vehicles, and this vapor may take some time to condense in the tank. This vapor has a relatively low ozone potential since it is composed primarily of butane. The trend in increased ozone potential with weathering did not occur with Phase 2 gasoline since it contained relatively few light components like butane and pentanes. Weathering and fuel temperature had almost no impact on the specific reactivity E85 since butane and ethanol have almost the same ozone potential, however on a per unit volume basis, the unweathered fuel has contains a greater vapor mass and subsequently has a higher ozone potential. The significant effect of weathering on the vapor mass concentration of E85 is caused by most of the fuel's vapor pressure being caused by 2-percent butane. As the liquid drum was emptied to 10 percent full, only 0.7 of the original 6.6 lb of butane in the drum would be available to form vapors. The saturated vapor concentration in the E85 drum was composed of about 0.2 lb of butane which is one third of the butane available in the drum. Therefore, fuel tank emptying reduced the mass concentration of the E85 vapors in spite of increased fuel temperature. The trend for methanol was less pronounced. The specific reactivity of M85 vapors did not change much with weathering.

Weathering would impact the composition and vapor pressure of vapors from vehicle fuel tanks. The specific reactivity of gasoline vapors would increase while the mass concentration would decrease somewhat. The effect of weathering would be most pronounced for ethanol blends with high butane contents. No weathering should occur in the fuel from underground storage tanks since the ullage is made up of vapors from vehicle fuel tanks which typically have higher vapor concentrations due to the higher vehicle fuel tank temperatures.

Variations in ambient temperature affected the results of the fuel vapor testing to various degrees. The ambient temperatures for vehicle tests were highest for the RFA tests while temperatures were fairly consistent with Phase 2 gasoline, M85 and E85. Tests on the fuel drum data covered a wider range of ambient temperatures and produced greater extremes in specific reactivity. The last two RFA tests resulted in higher liquid fuel temperatures and higher specific reactivities. These higher liquid temperatures do not reflect underground tank storage conditions. They probably represent the conditions in vehicle fuel tanks on hot days and floating roof storage tanks. Since no other fuels were tested at these temperatures, this data was not directly used to assess vapor compositions during hot driving conditions.

While the speciation data were not taken over completely controlled conditions, these tests provide valuable real world data. The compositions also can be used for calibrating vapor speciation models. Vapor speciation profiles were provided to Mobil Research and Development Corporation. These data can be used to better evaluate vapor composition as a function of fuel temperature.

Weathering played a role in some of the analyses. The E85 vapor mass was lower at a higher temperature point. This must have been caused by the selective evaporation of butane into the vapor space. The test series included measurements at various fuel drum levels.

ARB measured the composition of vapors from fuel drums and a vehicle fuel tank. The composition of the vapors depends on the composition and thermodynamic properties of the liquid mixture. Higher vapor pressure components tend to represent a larger fraction of the vapor space. Figure 2-9 shows the composition of vapors² from the vehicle tanks. Paraffins (including cycloparaffins) represent almost 90 percent of the vapor components from RF-A vapor. The majority of the paraffins are normal and isobutane which correspond to the 8.7 RVP of RF-A. For the assumed vapor pressure of 8.4 used in this study, there would be a slightly lower butane content of the fuel and fuel vapors; however no corrections to the composition have been made since the difference in RVP is relatively small. The vapor composition of Phase 2 gasoline contains less butane than RF-A. The fraction of olefins in Phase 2 vapor is slightly lower than that of RF-A. MTBE represents a larger fraction of the Phase 2 vapor than that of the liquid component. The higher MTBE fraction is consistent with the non-ideal behavior exhibited in Figure 2-3. RF-A has a lower average molecular weight than that of Phase 2 vapors as shown in Figure 2-10. The larger fraction of butane, which has a molecular weight of 58 contributes to the lower average molecular weight.

Hydrocarbon components represent a disproportional share of the vapor components for E85 and M85. About 25 percent of the vapor fraction of M85 is methanol with the balance composed of Phase 2 gasoline constituents. Most of the hydrocarbon vapors are butane. Olefins represent a

² The compositional breakdown of the vapors represents median values in Speciation Data Set 1.1. These are shown for illustrative purposes. Ozone potential in Section 3 is calculated from discrete speciations.

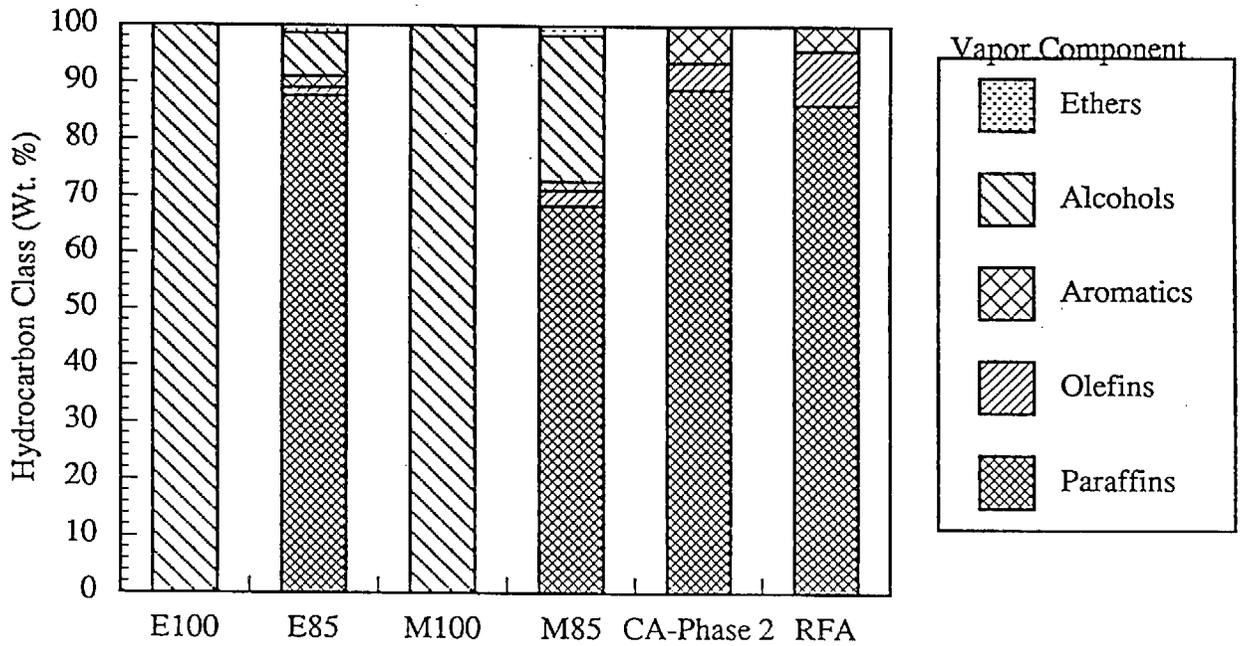


Figure 2-9. Composition of fuel vapors

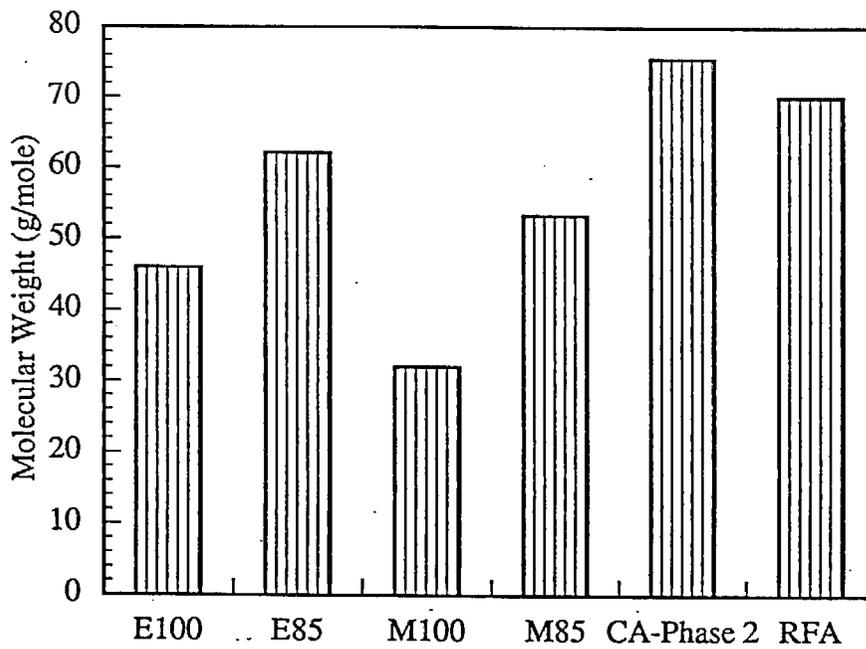


Figure 2-10. Average molecular weight of fuel vapors

proportionately lower fraction of the M85 vapor. Comparing the vapor concentrations of M85 vapors to those of Phase 2 gasoline, the Phase 2 gasoline contains about one-half the grams of olefin per gram of total butane.

Similarly, butane dominates the vapor composition for E85. Only about 10 percent of the E85 vapor mass is ethanol. The vapor composition of E85 is consistent with the higher molecular weight and lower vapor pressure of ethanol compared with methanol and the additional butane added to the E85 blend. Over one-half of the E85 vapor mass is normal butane. E100 and M100 vapors are composed of the same single component as the liquid mixture. While the speciation data were not taken over completely controlled conditions, it provides valuable real world data.

Mobil Research and Development Corporation performed equilibrium analyses based on the liquid fuel properties tested by ARB. These data can be used to better evaluate vapor composition as a function of fuel temperature. Calculations were made at a range of temperatures from 60 to 120°F. The calculations were based on an 80 percent full tank. A sensitivity study with a 20 percent full tank of Phase 2 gasoline was also performed. Tank fill level did not have a significant effect on predicted vapor compositions for Phase 2 gasoline. The equilibrium analyses were performed for RF-A, Phase 2 gasoline, M85 and E85 formulations that were tested by ARB, and M85 blended with 85.0 volume percent methanol. The vapor densities predicted by the model are shown in Figure 2-11. The vapor densities and vapor molecular weights are consistent with the trend for real world tests, except in the instances where weathering affected the fuel composition. The molecular weights predicted by the model increase with temperature for the gasolines and decreased with the alcohol blends as temperature increase.

2.8 GASEOUS FUELS — COMPRESSED NATURAL GAS, LIQUEFIED NATURAL GAS, AND HYDROGEN

Table 2-7 shows the properties of gaseous fuels. The natural gas compositions are an average of measurements provided by SoCalGas for gas delivered in Southern California. These values resemble closely the weighted average of natural gas composition for ten U.S. cities reported by GRI³ (Liss, 1991). While some natural gas supplies can vary significantly in composition, 80 percent (10th through 90th percentiles) of natural gas reported by GRI had a methane content within 88.5 and 96.4 percent. All gas that is currently sold in California is reported to have a relatively high methane content with typical methane contents above 92 percent which is within ARB's vehicle fuel specification of 88 percent (vol).

As natural gas demand increases to meet vehicle requirements, California will need to import more natural gas. This gas will probably be supplied from Canadian and Southwest U.S. sources (Thomason, 1993)⁴. Canadian gas has a higher methane content because hydrocarbons are extracted for LPG use. An average of 50-percent Canadian gas and 50-percent Southwest gas results in a mixture that is very close to the value in Table 2-7. Since the exact mix of incremental gas for vehicle fuel is difficult to predict and the composition in Table 2-7 is also representative of U.S. gas

³ Mean composition (vol%) for ten cities in the U.S. was methane: 93.2, ethane: 3.6, propane: 0.8, >C₄: 0.5, inerts 2.8.

⁴ Canadian gas composition (vol%) methane: 96.99, NMHC: 1.46. Southwestern gas composition (vol%) methane: 91.48, NMHC 6.33).

MIR Ozone Potential (g/gal)

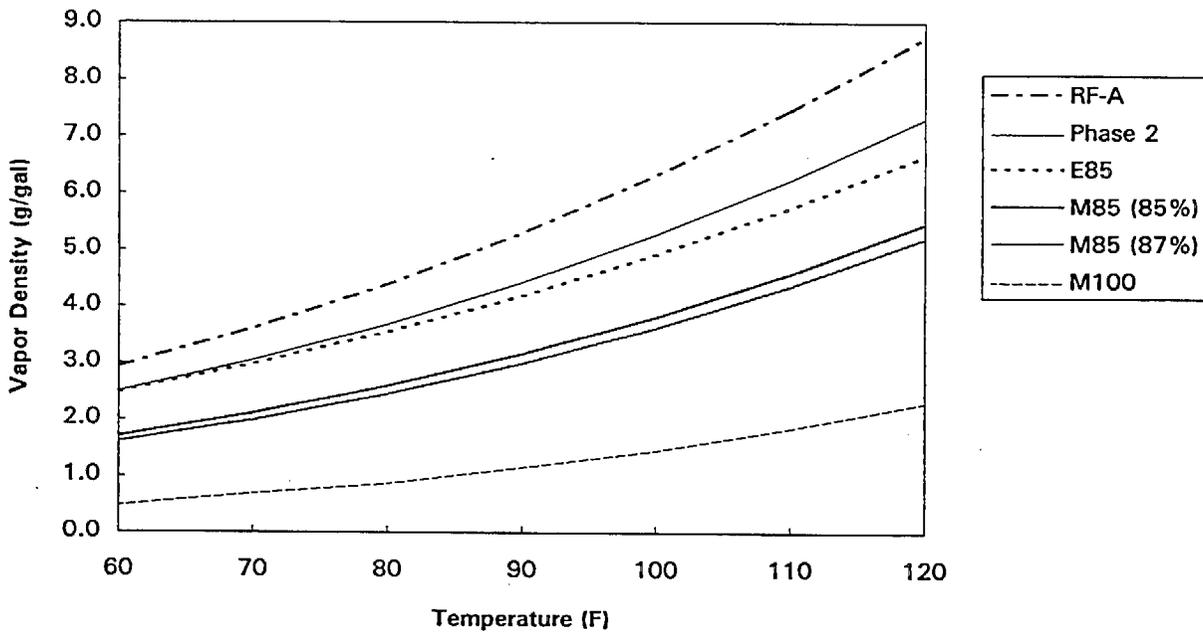
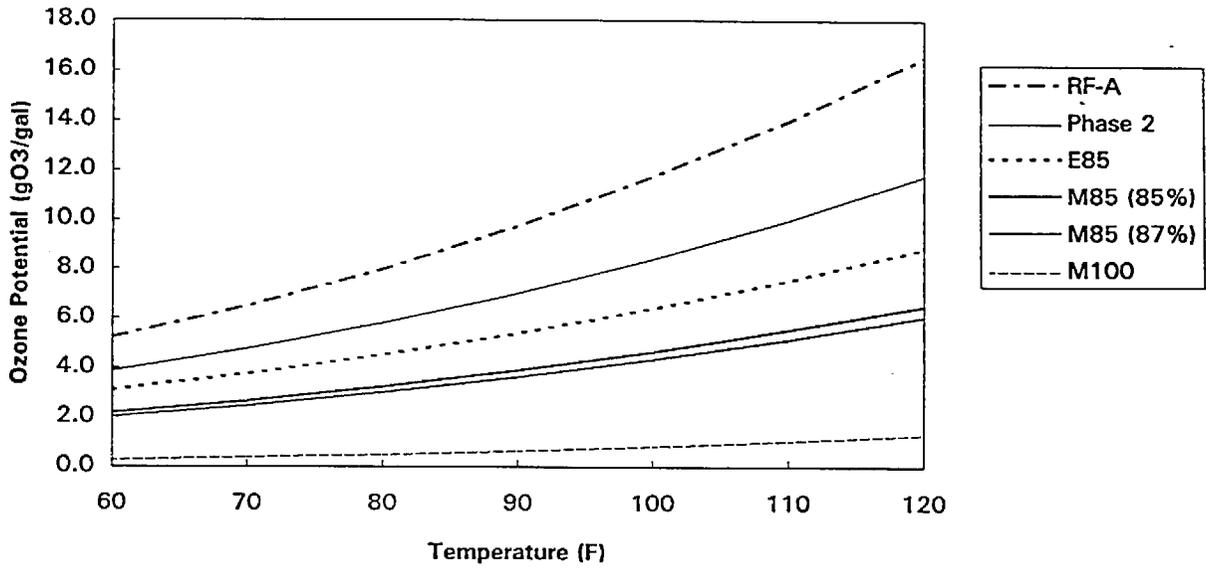


Figure 2-11. Model results for vapor pressure and density versus equilibrium temperature

Table 2-7. Properties of gaseous fuels

Property	Fuel ^a							
	CNG		LNG		LPG from petroleum		LPG from natural gas	
Carbon Content	0.736		0.740		0.82		0.818	
LHV ^b (Btu/lb)	20,300		20,800		19,770		19,770	
LHV (Btu/gal)	92,800 ^c		72,900		83,200		82,600	
Density (lb/gal)	4.6 ^c		3.5		4.21		4.18	
Composition	(vol %)	(wt %)	(vol %)	(wt %)	(vol %)	(wt %)	(vol %)	(wt %)
N ₂	1.6	2.6	0	0	0	0	0	0
CO ₂	1.0	2.5	0	0	0	0.0	0	0
CH ₄	93.2	86.4	94.2	88.7	0.05	0.03	0.1	0.06
C ₂ H ₆	3.1	5.4	3.1	5.5	0.5	0.37	2.0	1.48
C ₃ H ₈	0.7	1.8	0.7	1.8	94.15	93.9	97.0	97.5
C ₃ H ₆	0	0	0	0	2.3	2.3	0	0
C ₄ H ₁₀	0.4	1.3	0.4	1.4	3.0	3.4	0.9	1.0
C ₅ H ₁₂	0	0	0	0	0	0.0	0	0

^aCNG = Compressed natural gas, LNG = Liquefied natural gas,

LPG = Liquefied petroleum gas. LNG composition is based on CNG composition without N₂ and CO₂. LPG compositions were measured from fuel deliveries in Southern California. CNG composition is from SoCalGas.

^bLHV = Lower heating value.

^cPer 100 scf.

as well as possible new gas supplies to California, this composition is used throughout the study. The compositions in Table 2-7 are also shown as weight percent values so they can be treated consistently with liquid fuel compositions and to allow for calculation of ozone potential on a mass basis.

While some LNG producers make a very high percentage methane product (greater than 99 percent), the hydrocarbon composition of most LNG is the same as that of its natural gas feedstock. LNG does not contain CO₂ or water vapor since these are removed in the liquefaction process. LNG may contain some nitrogen which has a lower boiling point than that of LNG. Nitrogen weathers rapidly from LNG. Zero nitrogen was assumed for the LNG composition as some LNG contains little nitrogen. The principal effect of nitrogen on this analysis would be a proportional increase in tanker truck emissions.

The higher hydrocarbons can be present in the liquid LNG phase. The composition of LNG will vary in the fuel tank. If liquid is drawn from the fuel tank, heavy components will be consumed by the engine and will not accumulate in the tank. For vehicles that operate on LNG boil off, the heavier hydrocarbons will be concentrated in the fuel. Fuel cycle emissions are not affected by the

composition of the vehicle tank unless venting occurs. It may be more economical to design vehicles to operate on vaporized LNG rather than processing the LNG to a higher degree of purity (Powars, 1994) Therefore, the LNG composition used in this study is based on liquefying available natural gas without removing higher hydrocarbon components. Some LNG proponents advocate using high purity LNG which is over 99 percent methane in order to avoid operational problems with different engine types.

The composition of LPG represents typical analyses of fuel collected in Southern California (Unnasch, 1993). It is not clear whether petroleum-based or natural gas-based LPG would make up a large future fuel demand. Propane and butanes produced in oil refineries are now mostly converted to alkylate, used in the production of ethers, or sold into the chemical market; however, this LPG could be diverted to a higher value fuel market. Petroleum-based LPG contains several percent propylene while natural gas based LPG contains no propylene or other olefins. LPG compositions from petroleum and natural gas are shown in Table 2-7. Only refinery based LPG is considered in this study; however, the reader can use these data to investigate natural gas-based LPG.

The propylene (C_3H_6) content of the LPG composition in Table 2-7 suggests that the majority of this propane came from an oil refinery. Other samples had lower propylene content (less than 1 percent) which suggested that the product might be a blend of petroleum- and natural gas-based product. ARB's specification limits propylene to a maximum of 10 percent, which drops to 5 percent; however, observations of propylene in commercial LPG have shown lower levels. LPG is stored in pressure vessels. At 100°F the vapor pressure is about 190 psi.

Hydrogen for a vehicle fuel will be almost pure depending on how the hydrogen is produced and stored. Hydrogen that is produced from thermochemical processes such as the reforming of natural gas may contain traces of CO. This CO would be unacceptable to some types of fuel cells. Hydrogen that is produced from the electrolysis of water will be pure. When hydrogen is transported as a liquid, at -423°F, it is too cold to contain liquid phase contaminants. When vaporized, this hydrogen is also pure.

2.9 ELECTRICITY

Electrical energy in this study is reported in electric kWh. Thermal energy used in generating electricity and other fuels is reported in Btu. With this approach, electrical energy and thermal energy should not be confused. For conversion purposes, 1 kWh = 3412 Btu. Converting electrical energy to thermal energy incorporates the efficiency of the power conversion process. For example, if a diesel engine generator set operates with an efficiency of 29.3 percent, 10,000 Btu are required to produce 1 kWh.

SECTION 3

REACTIVITY OF HYDROCARBONS

In 1990, the ARB adopted the Low-Emission Vehicles and Clean Fuels regulations which apply to light- and medium-duty vehicles. These regulations recognize that the contribution of vehicle exhaust to ozone formation depends not only on the mass of the exhaust which is being emitted, but also on the composition of the non-methane organic gas (NMOG) exhaust. The lower ozone-forming potential of clean fuels compared to conventional gasoline is reflected in the Low-Emission Vehicle regulations through the use of reactivity adjustment factors. A reactivity adjustment factor is based on the ratio of the specific reactivity (g ozone/g NMOG) of the exhaust emissions of a low-emission vehicle operating on a clean fuel compared to the specific reactivity of the exhaust emissions of a low-emission vehicle operating on conventional gasoline. Compliance with the applicable low-emission vehicle standard is determined by multiplying the exhaust NMOG g/mi by the reactivity adjustment factor. This changes the previous requirement of equal non-methane hydrocarbon mass emissions by allowing a wide range of vehicle and fuel technologies to compete in the market place as long as they have equal ozone-forming potential. The regulations use the maximum incremental reactivity (MIR) scale developed by Professor William Carter of U.C. Riverside to determine ozone-forming potential of vehicle exhaust. In addition to the MIR scale, Professor Carter also developed the maximum ozone reactivity (MOR) scale for maximum ozone conditions. The MIR and MOR scales bracket the range of conditions where it is appropriate to define reactivity for hydrocarbon emission controls (Croes, 1991).

Table 3-1 shows the MIR and MOR ozone potential for individual organic species. The total ozone potential for an emission source is the sum of the $MIR \times$ mass emission rate for each component.

$$OP_{MIR} (gO_3/gal) = \sum (C_i \times MIR_i) \quad (3-1)$$

Where C_i represents the concentration (g/gal) for an individual species and MIR_i represents the ozone potential on the MIR scale for an individual species. The MOR ozone potential and vapor mixture molecular weight are calculated in a similar manner.

The average ozone potential for a given mix of organic compounds can be represented as the specific reactivity (SR). This value indicates the reactivity weighted emissions per mass of NMOG. For the MIR scale:

Table 3-1. Reactivity of organic compounds

Compound	MIR (gO ₃ /g)	MOR (gO ₃ /g)
<u>Normal Alkanes</u>		
Methane	0.0148	0.0100
Ethane	0.2500	0.1700
Propane	0.4800	0.3100
n-Butane	1.0200	0.6600
n-Pentane	1.0400	0.6800
n-Hexane	0.9800	0.6500
n-Heptane	0.8100	0.5300
n-Octane	0.6100	0.4100
n-Nonane	0.5400	0.3600
n-Decane	0.4700	0.3100
n-Undecane	0.4200	0.2800
n-Dodecane	0.3800	0.2500
<u>Branched Alkanes</u>		
2-Methylpropane	1.2100	0.7300
2,2-Dimethylpropane	0.3700	0.2200
2-Methylbutane	1.3800	0.8700
2,2-Dimethylbutane	0.8200	0.5100
2,3-Dimethylbutane	1.0700	0.6700
2-Methylpentane	1.5300	0.9000
3-Methylpentane	1.5200	0.9400
2,2,3-Trimethylbutane	1.3200	0.7900
2,2-Dimethylpentane	1.4000	0.8300
2,3-Dimethylpentane	1.5100	0.9000
2,4-Dimethylpentane	1.7800	0.9900
3,3-Dimethylpentane	0.7100	0.4600
2-Methylhexane	1.0800	0.6800
3-Methylhexane	1.4000	0.8300
2,2,4-Trimethylpentane	0.9300	0.5400
2,3,4-Trimethylpentane	1.6000	0.9200
2,2-Dimethylhexane	1.2000	0.7000
2,3-Dimethylhexane	1.3200	0.7800
2,4-Dimethylhexane	1.5000	0.8600
2,5-Dimethylhexane	1.6300	0.9300
3,3-Dimethylhexane	1.2000	0.7000
2-Methylheptane	0.9600	0.6000
3-Methylheptane	0.9900	0.6200
4-Methylheptane	1.2000	0.7000
2,3-Dimethylheptane	1.1400	0.6400
2,4-Dimethylheptane	1.3400	0.7500
3,5-Dimethylheptane	1.1400	0.6400
2,2,5-Trimethylhexane	0.9700	0.5800
2,3,5-Trimethylhexane	1.1400	0.6400
3-MethylOctane	1.1400	0.6400
4-MethylOctane	1.1400	0.6400
2,2-Dimethyloctane	1.0100	0.5600
2,4-Dimethyloctane	1.0100	0.5600

Table 3-1. Reactivity of organic compounds (continued)

Compound	MIR (gO ₃ /g)	MOR (gO ₃ /g)
<u>Cyclo Alkanes</u>		
Cyclopentane	2.3800	1.4100
Methylcyclopentane	2.8200	1.5500
Cyclohexane	1.2800	0.7400
1c,3-Dimethylcyclopentane	2.5500	1.3900
1t,2-Dimethylcyclopentane	1.8500	1.3900
Methylcyclohexane	1.8500	1.0000
Ethylcyclopentane	2.3100	1.3000
1c,2t,3-Trimethylcyclopentane	1.9400	1.0200
1c,2-Dimethylcyclohexane	1.9400	1.0200
1t,3-Dimethylcyclohexane	1.9400	1.0200
1c,3-Dimethylcyclohexane	1.9400	1.0200
1t,4-Dimethylcyclohexane	1.9400	1.0200
Ethylcyclohexane	1.9400	1.0200
<u>Alkenes</u>		
Ethene	7.2900	3.1600
Propene	9.4000	3.7700
1-Butene	8.9100	3.5100
2t-Butene	9.9400	3.7600
2c-Butene	9.9400	3.7600
2-Methylpropene	5.3100	1.9300
1-Pentene	6.2200	2.4600
2t-Pentene	8.8000	3.3000
2c-Pentene	8.8000	3.3000
2-Methyl-1-Butene	4.9000	1.9000
3-Methyl-1-Butene	6.2200	2.4600
2-Methyl-2-Butene	6.4100	2.3000
1-Hexene	4.4200	1.7400
2t-Hexene	6.6900	2.5000
2c-Hexene	6.6900	2.5000
3t-Hexene	6.6900	2.5000
3c-Hexene	6.6900	2.5000
2-Methyl-1-Pentene	4.4200	1.7400
3-Methyl-1-Pentene	4.4200	1.7400
4-Methyl-1-Pentene	4.4200	1.7400
2-Methyl-2-Pentene	6.6900	2.5000
3-Methyl-2t-Pentene	6.6900	2.5000
4-Methyl-2c-Pentene	6.6900	2.5000
4-Methyl-2t-Pentene	6.6900	2.5000
3,3-Dimethyl-1-Butene	4.4200	1.7400
1-Heptene	3.4800	1.3800
2c-Heptene	5.5300	2.0700
2t-Heptene	5.5300	2.0700
3t-Heptene	5.5300	2.0700
3-Ethyl-2c-Pentene	5.5300	2.0700
2,3-Dimethyl-2-Pentene	5.5300	2.0700

Table 3-1. Reactivity of organic compounds (continued)

Compound	MIR (gO ₃ /g)	MOR (gO ₃ /g)
<u>Alkenes (concluded)</u>		
3-Methyl-1-Hexene	3.4800	1.3800
2-Methyl-2-Hexene	5.5300	2.0700
3-Methyl-3t-Hexene	5.5300	2.0700
1-Octene	2.6900	1.0700
2c-Octene	5.2900	1.9900
2t-Octene	5.2900	1.9900
4t-Octene	5.2900	1.9900
2,4,4-Trimethyl-1-Pentene	2.6900	1.0700
2,4,4-Trimethyl-2-Pentene	5.2900	1.9900
1-Nonene	2.2300	0.8900
Propadiene	7.2900	2.3400
1,3-Butadiene	10.8900	4.1600
2-Methyl-1,3-Butadiene	9.0800	3.4100
Cyclopentadiene	7.6600	3.5000
Cyclopentene	7.6600	2.7800
3-Methylcyclopentene	5.6700	2.2000
Cyclohexene	5.6700	2.2000
3-Methyl-2c-Pentene	6.6900	2.5000
3,4-Dimethyl-1-Pentene	3.4800	1.3800
<u>Alkynes</u>		
Ethyne	0.5000	0.3300
Propyne	4.1000	2.1700
1-Butyne	9.2400	3.6400
2-Butyne	9.2400	3.6400
<u>Aromatic Hydrocarbons</u>		
Benzene	0.4200	0.1400
Toluene	2.7300	0.6300
Ethylbenzene	2.7000	0.6300
o-Xylene	6.4600	1.9500
m&p-Xylenes	7.3800	2.3000
n-Propylbenzene	2.1200	0.4900
i-Propylbenzene	2.2400	0.5200
1-Methyl-3-ethylbenzene	7.2000	2.1600
1-Methyl-4-ethylbenzene	7.2000	2.1600
1-Ethyl-2-methylbenzene	7.2000	2.1600
1,2,3-Trimethylbenzene	8.8500	2.6700
1,2,4-Trimethylbenzene	8.8300	2.6700
1,3,5-Trimethylbenzene	10.1200	3.0500
Indan (C ₉ H ₁₀)	1.0600	0.1400
n-Butylbenzene	1.8700	0.4300
s-Butylbenzene	1.8900	0.4400
1,2-Diethylbenzene	6.4500	1.9400
1,3-Diethylbenzene	6.4500	1.9400
1,4-Diethylbenzene	6.4500	1.9400
1,2,3,4-Tetramethylbenzene	9.0700	2.7300
1,2,3,5-Tetramethylbenzene	9.0700	2.7300

Table 3-1. Reactivity of organic compounds (concluded)

Compound	MIR (gO ₃ /g)	MOR (gO ₃ /g)
<u>Aromatic Hydrocarbons</u>		
1,2,4,5-Tetramethylbenzene	9.0700	2.7300
1-Methyl-4-Isobutylbenzene	5.8400	1.7600
Styrene	2.2200	-0.3000
Naphthalene	1.1800	0.0900
4-Ethyltoluene	4.4900	1.8100
<u>Aromatic Oxygenates</u>		
Benzaldehyde	-0.5500	-1.2300
p-Tolualdehyde	3.3200	-1.0900
<u>Alcohols</u>		
Methanol	0.5600	0.2800
Ethanol	1.3400	0.7300
<u>Aldehydes</u>		
Formaldehyde	7.1500	2.0800
Acetaldehyde	5.5200	2.1700
Propionaldehyde	6.5300	2.4900
Acrolein	6.7600	2.5800
n-Butyraldehyde	5.2600	2.0100
Crotonaldehyde	5.4200	2.0700
Pentanaldehyde	4.4100	1.6800
Hexanaldehyde	3.7900	1.4500
<u>Ethers</u>		
Methyl t-Butyl Ether	0.6200	0.4000
Ethyl t-Butyl Ether	1.9800	1.0300
<u>Ketones</u>		
Acetone	0.5600	0.2000
Butanone	1.1800	0.5500

$$SR_{MIR} = \frac{\sum (m_i \times MIR_i)}{\sum m_i} \quad (3-2)$$

When calculating SR values, mass fractions, m_i , or concentrations, C_i , can be used to weight MIR or MOR ozone potentials.

Specific reactivities were calculated for NMOG emissions. Methane is tracked separately and its incremental ozone potential can be calculated from information in Section 6. Table 3-2 gives an example of the calculation of a specific reactivity. The specific reactivity is used to determine the

Table 3-2. Example of applying reactivity factor to NMOG and methane emission factor

Emission Source — Natural Gas Reciprocating Engines	Value
NMOG emission rate (g/bhp-hr)	0.45
CH ₄ emission rate (g/bhp-hr)	4.42
NMOG specific reactivity profile	1001
Specific MIR ^a (gO ₃ /gNMOG)	0.41
Specific MOR ^b (gO ₃ /gNMOG)	0.18
Reactivity weighted ozone potential (gO ₃ /bhp-hr)	
MIR x NMOG + 0.0148 x CH ₄	0.25
MOR x NMOG + 0.0100 x CH ₄	0.125

^aMIR = Maximum incremental reactivity.

^bMOR = Maximum ozone reactivity.

ozone potential per unit of fuel. For each emission source, the ozone potential is determined from the product of mass emissions per unit of fuel and the specific reactivity for that emission source.

Several trends can be identified in the ozone potential factors in Table 3-1. Paraffins (alkanes) tend to have low ozone potential on the order of 1 g O₃/g (MIR). Methane and propane fall into this category. The ozone potential of methane is so low it is often treated in a category of non-reactive hydrocarbons. Ozone potentials for olefins (alkenes), aldehydes, and heavy aromatic compounds are on the high end of the range (3 to 9 g O₃/g). The ozone potentials for methanol and MTBE are lower than those of most paraffins while the ozone potentials for ethanol and ETBE are about twice those of methanol but still lower than many hydrocarbon mixtures.

ARB's analysis of fuels and vapors provided data for the determination of ozone potential. Figures 3-1 and 3-2 show the MOR and MIR ozone potential of liquid fuels that were tested by ARB. Aromatics represent the largest contribution towards ozone potential in RF-A. Olefins contribute significantly to the ozone potential of the fuel given their low (<10 percent) mass fraction. Unidentified components represent about 0.5 percent of the RF-A and Phase 2 gasoline compositions. In addition, some specific compounds (about 5 percent) can only be identified by hydrocarbon class. The unidentified compounds are grouped near paraffins and aromatics in the GC data. The unknown components were assigned the average ozone potential of the identified components. The unknown fraction of M85 and E85 were relatively small. The ozone potential of Phase 2 gasoline is reduced compared to RF-A because of the lower aromatics and olefins which are displaced to some extent by MTBE and saturated hydrocarbons. The reduced ozone potential of Phase 2 gasoline was accomplished while also reducing butane, even though this is a low ozone potential component in RF-A. The ozone potential of M85 and E85 includes the proportional share from the Phase 2 gasoline component. The ozone potentials of E100 and M100 are reflected in the E85 and M85 blends.

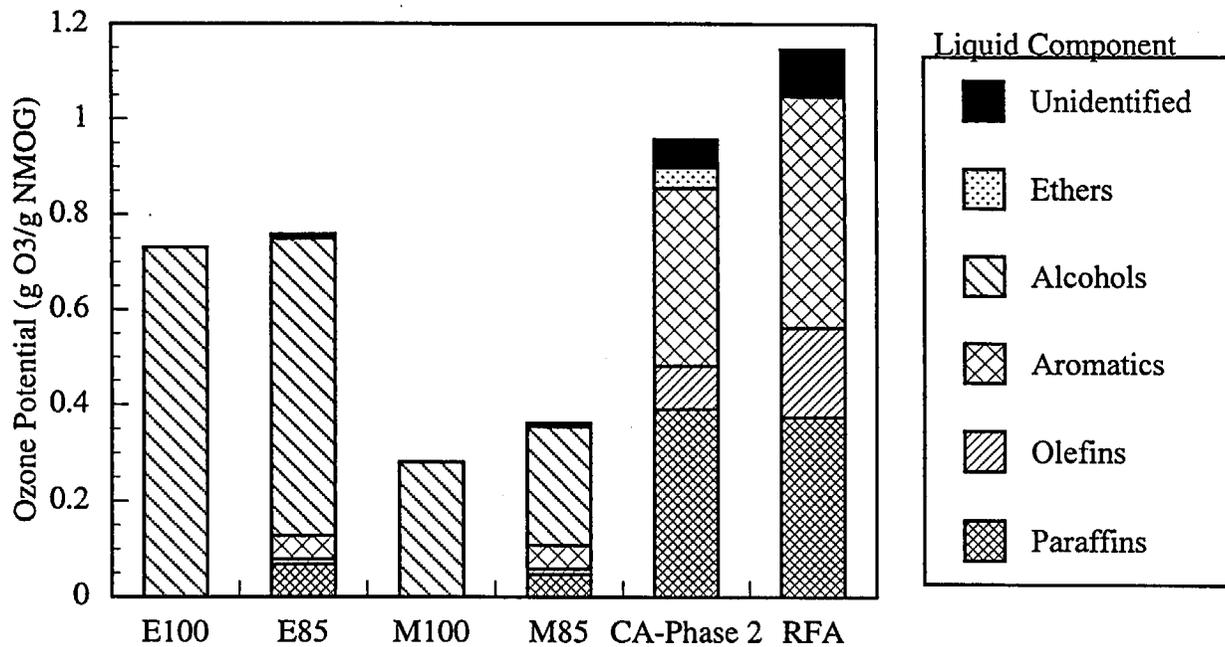


Figure 3-1. Specific MOR reactivity for liquid fuels

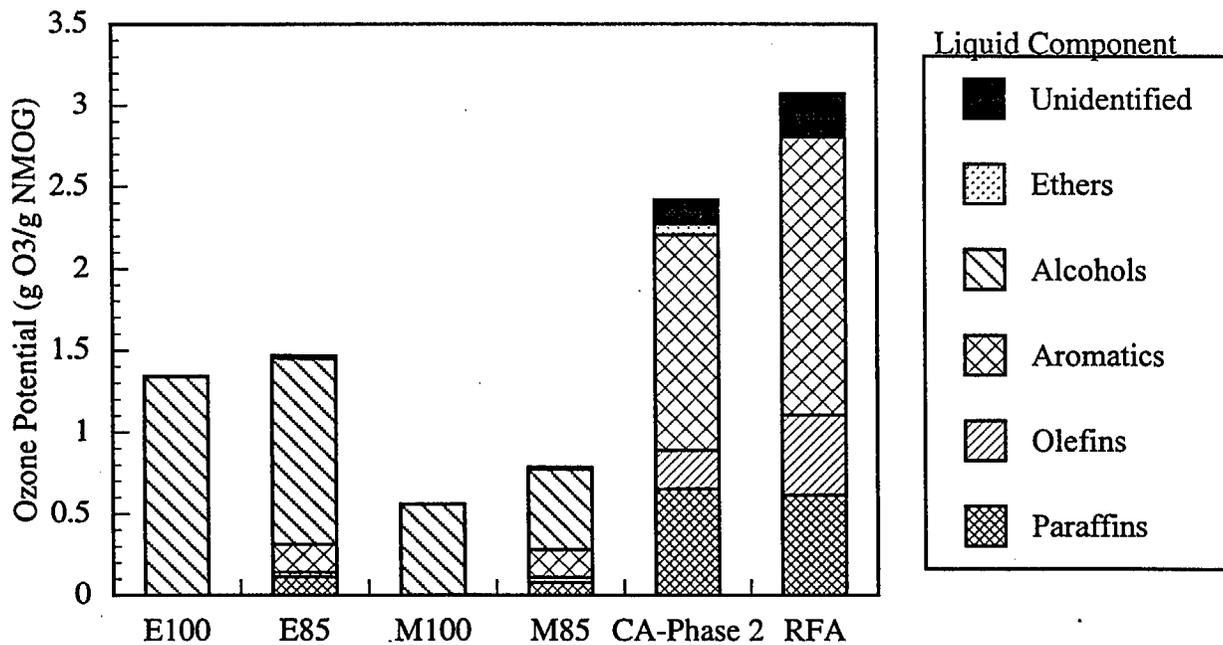


Figure 3-2. Specific MIR reactivity for liquid fuels

The ozone potential of fuel vapors relates to the vapor composition discussed in Section 2.2. Figures 3-3 and 3-4 show the MOR and MIR ozone potential for vehicle fuel tanks close to 80 °F. Butane and pentane represent the bulk of the ozone potential from the gasoline blends. Since the E85 fuel was volatility adjusted with butane, about 80 percent of its ozone potential is due to butane. Olefins contribute less (on an absolute basis and in proportion to paraffins) to the total ozone potential in M85 vapors than in Phase 2 gasoline vapors. A relatively small fraction of alcohols and MTBE is found in the M85 and E85 vapors. The net result is a low contribution towards ozone potential for these components.

The specific reactivity by component class was based on a single vapor sample to illustrate the source of ozone potential. The variation in samples from RF-A was large, presumably due to a range in temperature conditions and resulting variations in butane content in the vapor space. The total ozone potential depends on vapor mass concentration, therefore, the net ozone potential in g/gal of Phase 2 gasoline will be lower than that of RF-A.

The results of ARB's liquid and vapor speciation tests are shown in Tables 3-3 and 3-4. The compositions for RF-A and Phase 2 gasoline consist of about 8 percent unidentified components. The ozone potential of these components was assumed to be the same as that of the average of the identified components. The specific reactivity based on the MIR and MOR scales, as well as the vapor molecular weight are calculated for the different test points. The corresponding fuel temperatures and fuel tank pressures and individual speciations are provided in Speciation Data Set 1.0. The vapor speciation results indicate that the majority of M85 and E85 vapors are hydrocarbons. The specific reactivity of M85 vapors is slightly more than twice that of M100 and about 30 percent below that of Phase 2 gasoline. These results are considerably different from those

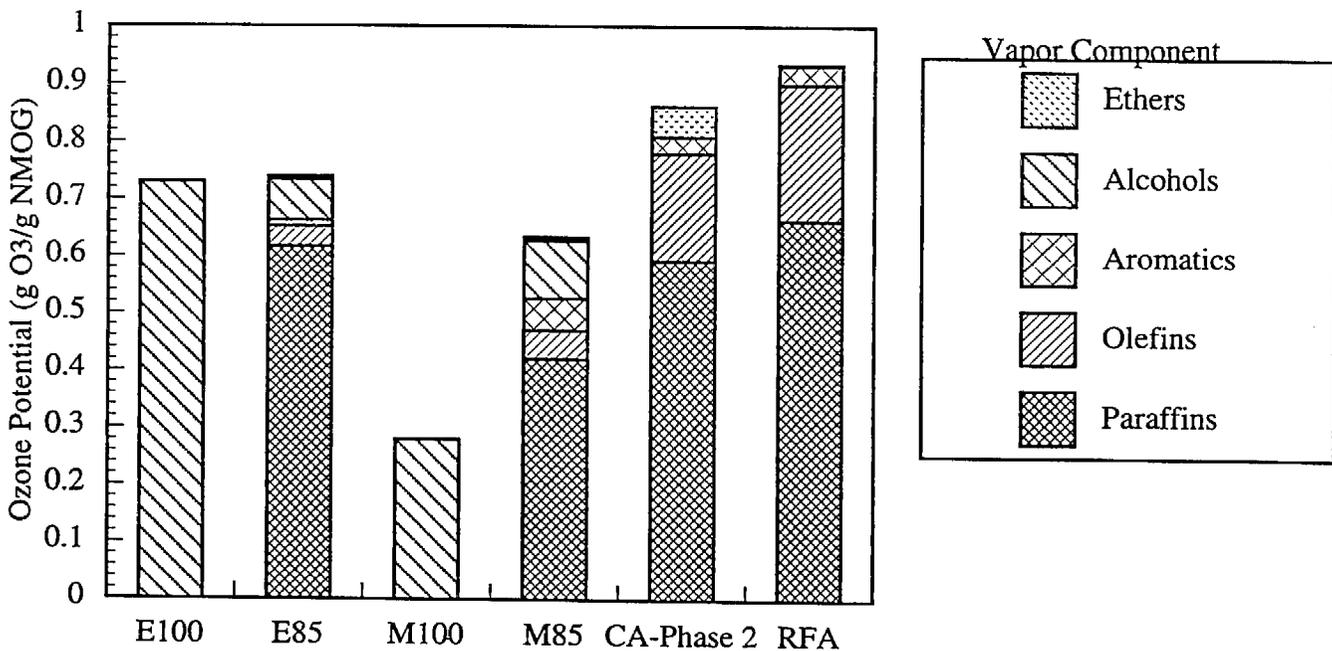


Figure 3-3. Specific MOR reactivity of fuel vapors

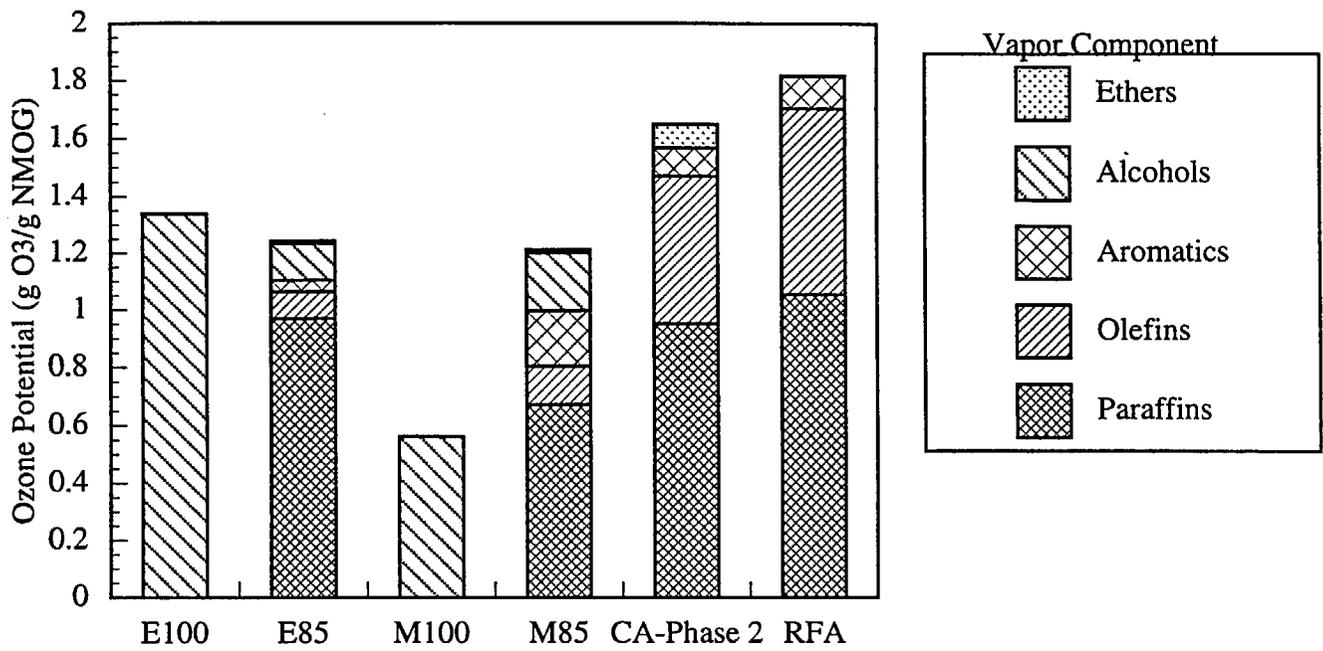


Figure 3-4. Specific MIR reactivity of fuel vapors

Table 3-3. Liquid fuel speciation results

Test ID	Fuel	Specific Reactivity (gO ₃ /g NMOG)		Molecular Weight	% Identified
		MIR	MOR		
DHA049	Phase 2	2.4356	0.9622	97.13	93.52
DHA052	Phase 2	2.4062	0.9550	96.91	93.33
DHA050	RF-A	3.1116	1.1603	92.54	90.52
DHA054	RF-A	3.1876	1.1788	92.95	91.67
DHA055	M85	0.7856	0.3611	34.74	99.39
DHA068	E85	1.4668	0.7576	49.49	99.34

Table 3-4. Vapor concentrations and ozone potential for vehicle and fuel drum tests, July 1994

Fuel Type	Test ID	Tank Level (%)	Vapor Temperature (F)	Liquid Temperature (F)	Average Temperature (F)	Molecular Weight (g)	Sample Conc. g/gal sample	Specific MIR g O ₃ /g NMOG	Reactivity MOR g O ₃ /g NMOG	Ozone Potential g O ₃ /gal
Phase 2 Drum	VR5	100	94	75	84.5	77.10	3.56	1.76	0.86	6.27
	VR13	40	99	75	87	76.82	3.48	1.83	0.90	6.36
	VR17	10	101	84	92.5	75.69	3.24	1.58	0.85	5.11
Phase 2 Vehicle	VR21	100	93	90	91.5	77.58	4.32	1.83	0.90	7.89
	VR25	80	82	82	82	75.53	3.29	1.78	0.93	5.85
	VR29	40	89	96	92.5	75.87	3.54	1.67	0.86	5.89
	VR37	80	74	69	71.5	66.50	2.65	1.74	0.92	4.62
RFA Drum	VR45	40	94	68	81	68.25	3.73	1.77	0.93	6.60
	VR47	10	100	76	88	72.92	3.86	2.14	1.07	8.25
	VR49	10	101	81	91	70.52	5.34	2.43	1.01	12.98
	VR51	80	93	91	92	72.92	5.35	2.43	1.07	13.00
RFA Vehicle	VR53	40	74	78	76	70.08	3.55	1.85	0.95	6.56
	VR55	10	77	82	79.5	71.84	3.13	1.98	0.98	6.20
	VR59	40	84.3	70.7	77.5	50.86	2.60	1.14	0.64	2.97
M85 Drum	VR61	10	109	85.5	97.25	49.24	2.43	1.21	0.63	2.93
	VR83	10	67	68	67.5	52.52	1.98	1.21	0.67	2.40
	VR63	80	77.2	73.8	75.5	53.35	2.72	1.21	0.67	3.30
M85 Vehicle	VR67	10	74.7	77.6	76.15	52.34	1.98	1.22	0.67	2.42
	VR69	80	76.4	70.6	73.5	61.68	2.83	1.23	0.74	3.48
E85 Drum	VR71	40	99.2	73.5	86.35	61.69	2.02	1.24	0.74	2.51
	VR73	10	99.3	82.1	90.7	61.92	2.00	1.25	0.74	2.51
	VR75	80	77	75	76	62.15	2.99	1.29	0.75	3.86
E85 Vehicle	VR77	40	81	84	82.5	61.09	3.45	1.26	0.74	4.35
	VR79	10	74	83	78.5	63.04	2.54	1.25	0.75	3.19

in Furey, 1986, where the reactivity of the vapor composition was less than 50 percent of the liquid composition. This result may be due a higher vapor pressure fuel which contained proportionately more butane in its vapor composition. The reactivity of the vapor space is similar to the reactivity of the vapors emitted from diurnal evaporative tests.

The molecular weight of the vapors can be used to determine the vapor space mass concentration for a given true vapor pressure of a fuel tank. ARB also measured the mass concentration from the vapor samples. The combination of vapor pressure, molecular weight, and specific reactivity are used to determine the net ozone potential for fuel vapors in Section 5. Calculations based on the vapor mass fraction and ozone potential are shown in Section 5 for refueling emissions.

Figures 3-5 and 3-6 show the specific reactivity and per gallon ozone potential for the ARB vapor tests. These figures illustrate the effect of real world fueling conditions and provide some insight into the effect of temperature on ozone potential.

The ozone potential of NMOG emissions depends upon the fuel storage conditions and the source of emissions. The largest impact on ozone potential is the vapor density. Specific reactivity varies with fuel temperature and weathering to some degree as predicted by the Mobile model. This effect is fairly small for all fuels except M85 where the specific reactivity drops at elevated temperatures. For this study, the specific reactivity was not adjusted for temperature as there was very little temperature dependent data. The ozone potential of spilled fuel should be the same as that of the liquid fuel since all of the liquid fuel will eventually evaporate. Actual tank conditions will be higher on hot summer days; however, the data for these temperature conditions is limited. Higher temperatures should increase the ozone potential of all fuels on a g/gal basis and should be investigated further.

Additional vapor speciation tests were performed by ARB in August 1995. The purpose of these tests was to investigate the following issues:

- Differences in ozone potential between model results and speciation results
- Relatively high fraction of ozone potential that was attributed to aromatics in July 1994 speciation results for Phase 2 gasoline
- Potential for mists entering the sampling line and not properly representing the composition of vapors that are released during vehicle fueling
- Differences between equilibrium compositions and vehicle fuel tank compositions
- Effect of analytical methods on speciation results

These issues were addressed in the 1995 tests by adopting the following approach:

- Measure vapor composition from fuel in jar at equilibrium, vehicle fuel tank, and from displaced vapors during refueling
- Use nitrogen to dilute sample for GC analysis

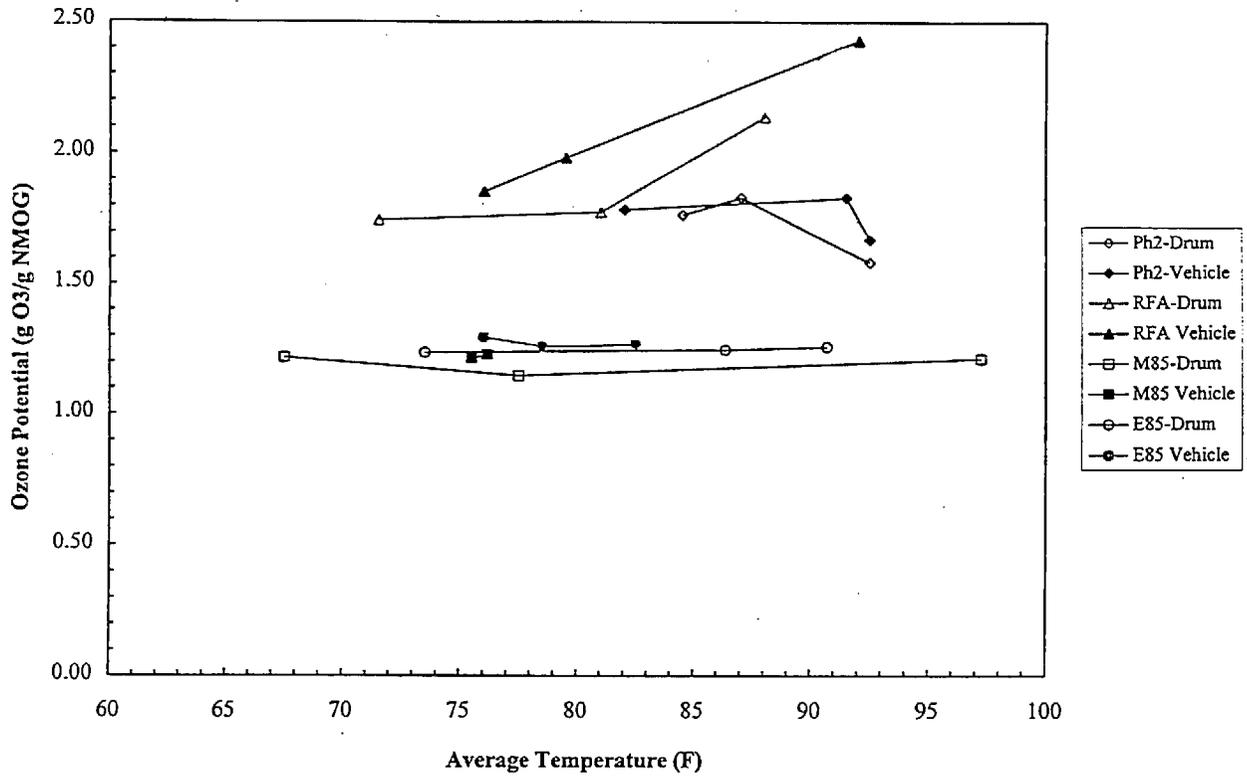


Figure 3-5. Specific reactivity (MIR) versus average temperature

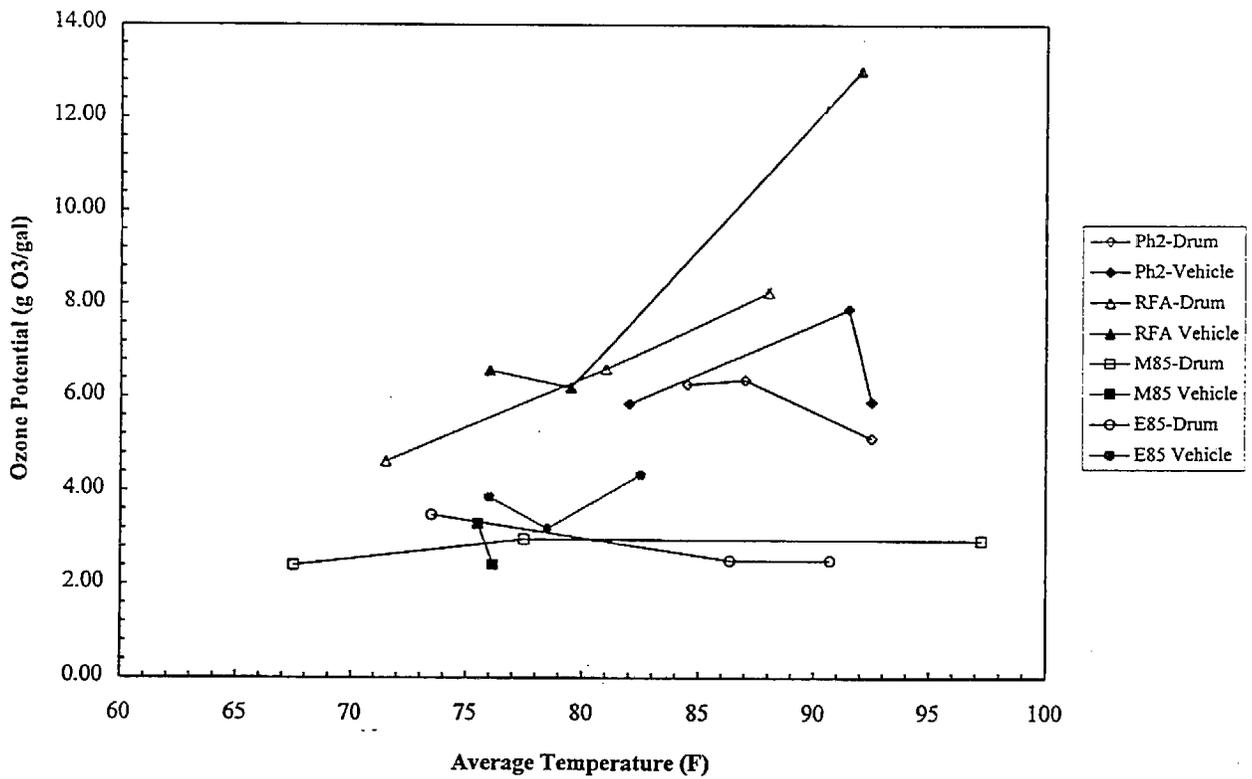


Figure 3-6. Ozone potential (MIR) versus average temperature volume basis

- Dilute a limited number of samples in an evaporative measurement SHED in order to assess the accuracy of prior tests using the SHED dilution technique
- Sample vapors during vehicle refueling using a probe that collects displaced vapors rather than sampling from inside the fuel tank in order to assess the potential for mists affecting the vapor composition

Table 3-5 summarizes the test conditions, vapor density, specific reactivity, and ozone potential for the August 1995 tests. Figures 3-7 through 3-10 show the specific reactivity and reactivity of Phase 2 gasoline and RF-A vapors, identified by hydrocarbon class. The following observations can be drawn from these data:

- The specific reactivity for Phase 2 gasoline determined from vapor measurements is higher than that predicted by the model results for both equilibrium type jar tests as well as vehicle vapor tests
- There is significant test to test variation in the contribution of aromatics towards specific reactivity, both in the jar tests and the fuel tank tests
- The contribution of aromatics towards Phase 2 gasoline specific reactivity is substantially higher in the July 1994 tests than in the August 1995 tests (see Appendix A)
- The specific reactivity for some of the RF-A data were significantly higher than the mean. These data appear to correspond to higher temperature conditions and should be investigated further.
- The Phase 2 vapor samples show little difference in the contribution to specific reactivity by hydrocarbon class
- Significant variation in the contribution of hydrocarbon type towards specific reactivity can be observed in the RF-A vapor data. Some of this variation may be due to temperature effects. These refueling and jar (TR- and J-) data points had less variation in the contribution of aromatics towards specific reactivity.
- Conclusions regarding which specific reactivity values and which ozone potential values to use in this study are based on the August 1995 data

The results of the vapor composition modeling performed by Mobil Research and Development Corporation (MRDC) are shown in Figures 3-11 and 3-12. The ozone potential is shown on a g O₃/gal basis (M100 was based on vapor pressure data). In general, the model results are in good agreement with ARB's measurements on a specific reactivity basis (g O₃/g NMOG) and the model indicates that ozone potential does not vary substantially over a temperature range from 60 to 120°F. Increases in specific reactivity shown in Figure 3-5 are not reflected in the model results and warrant further investigation.

Table 3-6 shows the specific reactivity for liquid and vapor emissions used in this study. The values used in this study for gasoline correspond to the August 1995 vehicle tank vapor data which was collected under improved sampling and analysis conditions. The 1994 vehicle tank vapor data

Table 3-5. Vapor concentrations and ozone potential for jar and vehicle tests, August 1995

Fuel Type	Test ID	Tank Level (%)	Fuel Temperature (F)	Molecular Weight (g/mol)	Sample Conc. (g/gal)	MIR (g O ₂ /g NMOG)	MOR (g O ₂ /g NMOG)	IR-Ozone Potential (g/gal)	OR-Ozone Potential (g/gal)
Phase 2 Jar	J-PH2-1A		75	76.23	3.96	1.59	0.85	6.32	3.37
	J-PH2-3		75	76.43		1.75	0.89		
	J-PH2-4		75	78.52		1.79	0.90		
	J-RFA-1A		75	70.59	4.73	1.72	0.91	8.13	4.31
RFA Jar	J-RFA-3		75	70.73		1.83	0.94		
	J-RFA-4		75	71.17		1.84	0.94		
	S10-RFA-3	10	74	70.04	2.36	1.69	0.90	3.98	2.13
	S10-RFA-4	10		70.96	2.41	1.79	0.93	4.33	2.23
RFA Tank SHED-Dilut.	S90-RFA-3	90	93	69.33	4.67	1.72	0.92	8.02	4.29
	S90-RFA-4	90		69.13	4.63	1.71	0.92	7.90	4.24
	SR-RFA-3	refuel	78	71.71	3.55	1.87	0.95	6.66	3.38
	SR-RFA-4	refuel		70.69	3.61	1.80	0.93	6.48	3.37
Phase 2 Tank	T10-PH2-1	10		76.62	3.96	1.61	0.85	6.37	3.38
	T10-PH2-2	10		76.98	4.02	1.63	0.86	6.55	3.44
	T10-PH2-3	10		77.48	3.28	1.61	0.85	5.29	2.78
	T10-PH2-4	10		78.10	3.62	1.64	0.85	5.95	3.09
	T90-PH2-1	90		77.64	6.04	1.63	0.86	9.82	5.17
	T90-PH2-2	90		78.48	5.95	1.64	0.86	9.75	5.09
	T90-PH2-3	90		76.02	6.43	1.60	0.85	10.27	5.48
	T90-PH2-4	90		75.72	6.35	1.61	0.86	10.21	5.45
RFA Tank	TR-PH2-1	refuel		77.38		1.68	0.87		
	TR-PH2-2	refuel		76.71		1.66	0.87		
	TR-PH2-3	refuel		76.60		1.64	0.86		
	TR-PH2-4	refuel		76.57		1.64	0.86		
	T10-RFA-1	10		72.53	6.37	1.79	0.92	11.42	5.89
	T10-RFA-2	10		72.78	6.33	1.77	0.92	11.20	5.79
	T10-RFA-3	10		71.39	5.24	1.79	0.92	9.36	4.83
	T10-RFA-4	10		71.12	5.01	1.77	0.92	8.89	4.61
RFA Tank	T90-RFA-1	90		72.94	5.85	1.86	0.94	10.87	5.52
	T90-RFA-2	90		71.70	4.85	1.80	0.93	8.72	4.51
	T90-RFA-3	90		72.05	4.34	1.87	0.95	8.12	4.11
	T90-RFA-4	90		80.21	1.54	2.33	1.04	3.58	1.61
	TR-RFA-1	refuel		70.87	5.58	1.78	0.93	9.95	5.19
	TR-RFA-2	refuel		70.74	5.42	1.79	0.93	9.68	5.05
	TR-RFA-3	refuel		70.85	4.33	1.83	0.94	7.91	4.06
	TR-RFA-4	refuel		70.60	4.33	1.83	0.94	7.90	4.05

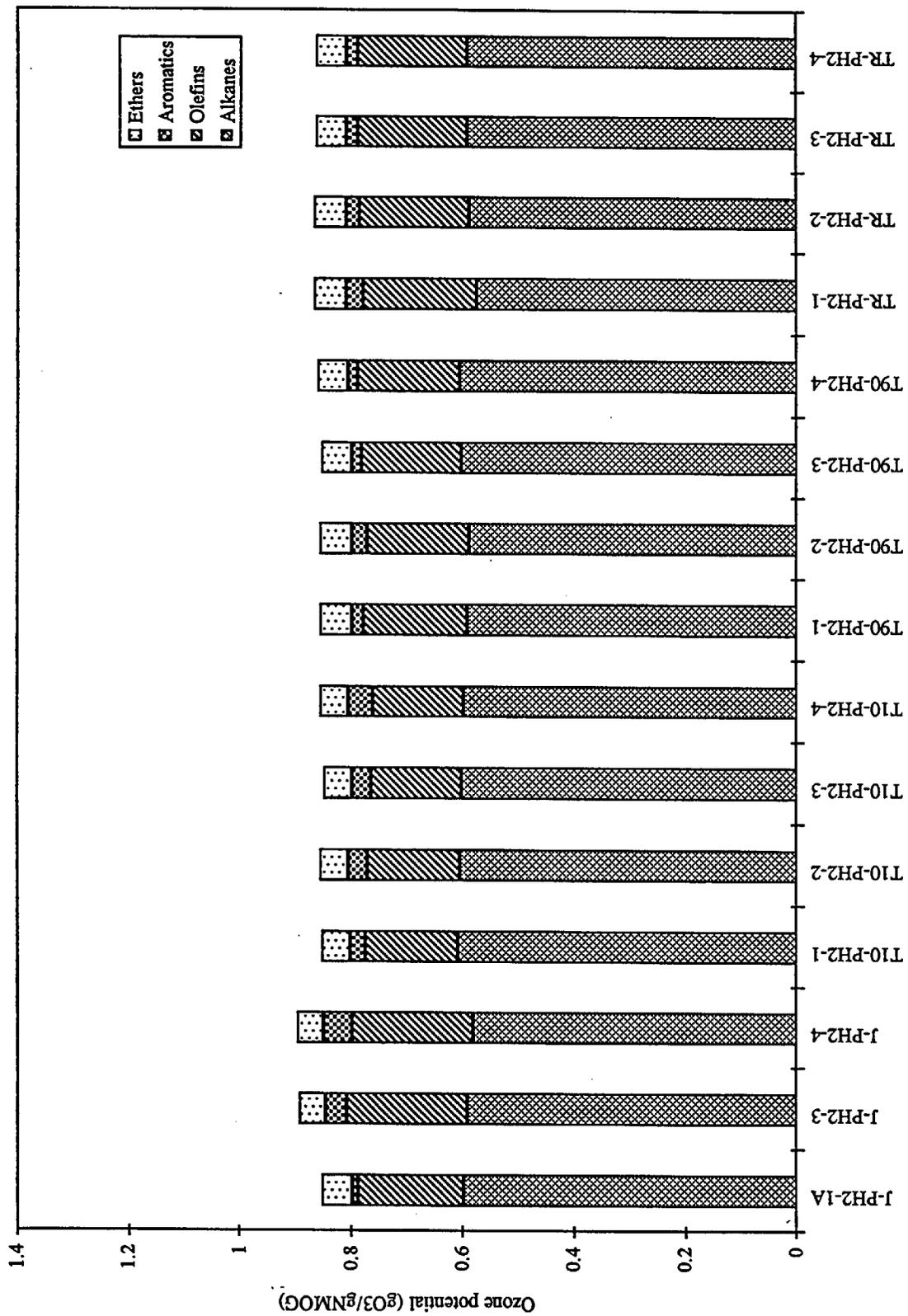


Figure 3-7. Specific MOR reactivity for Phase 2 gasoline

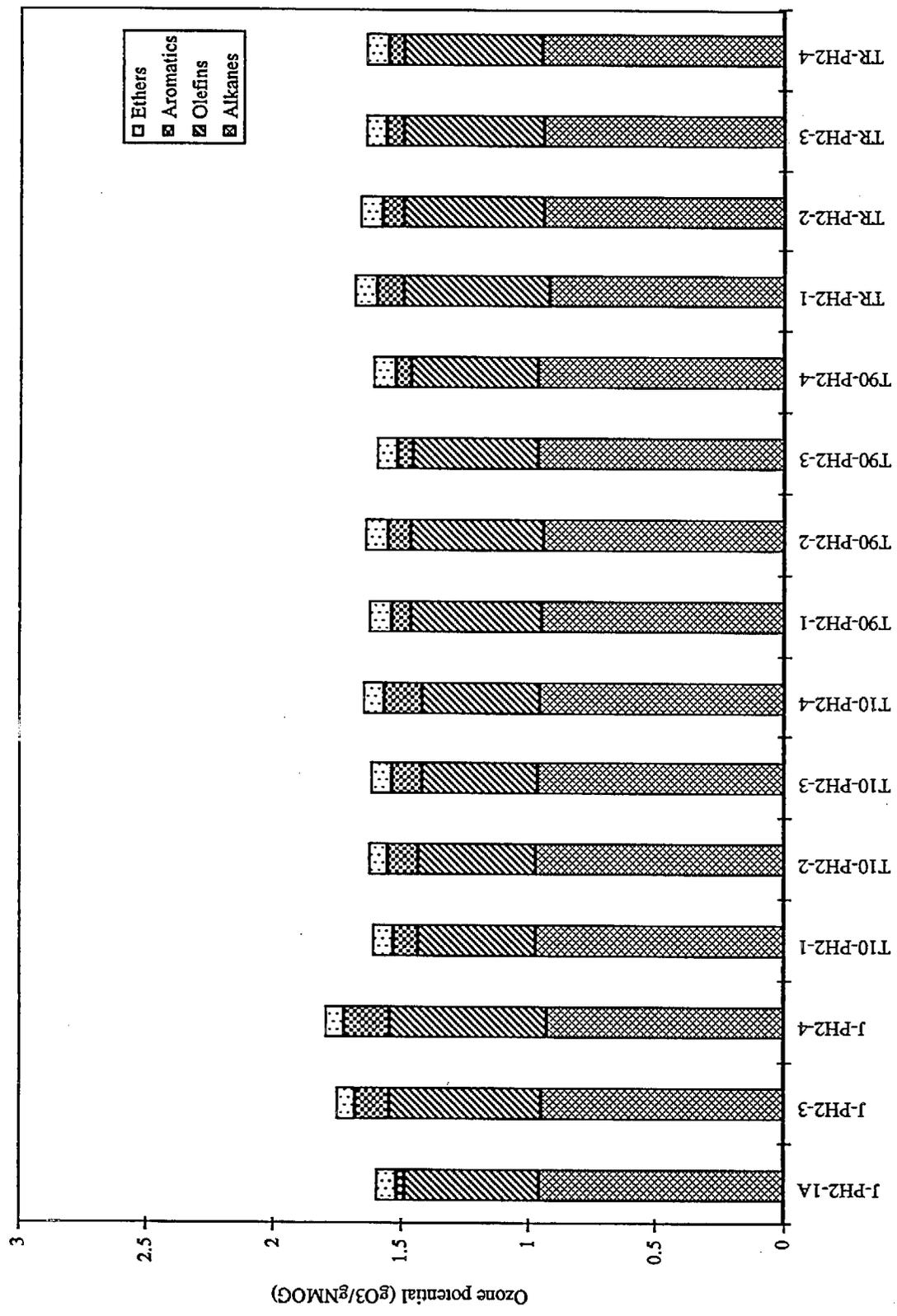


Figure 3-8. Specific MIR reactivity for Phase 2 gasoline

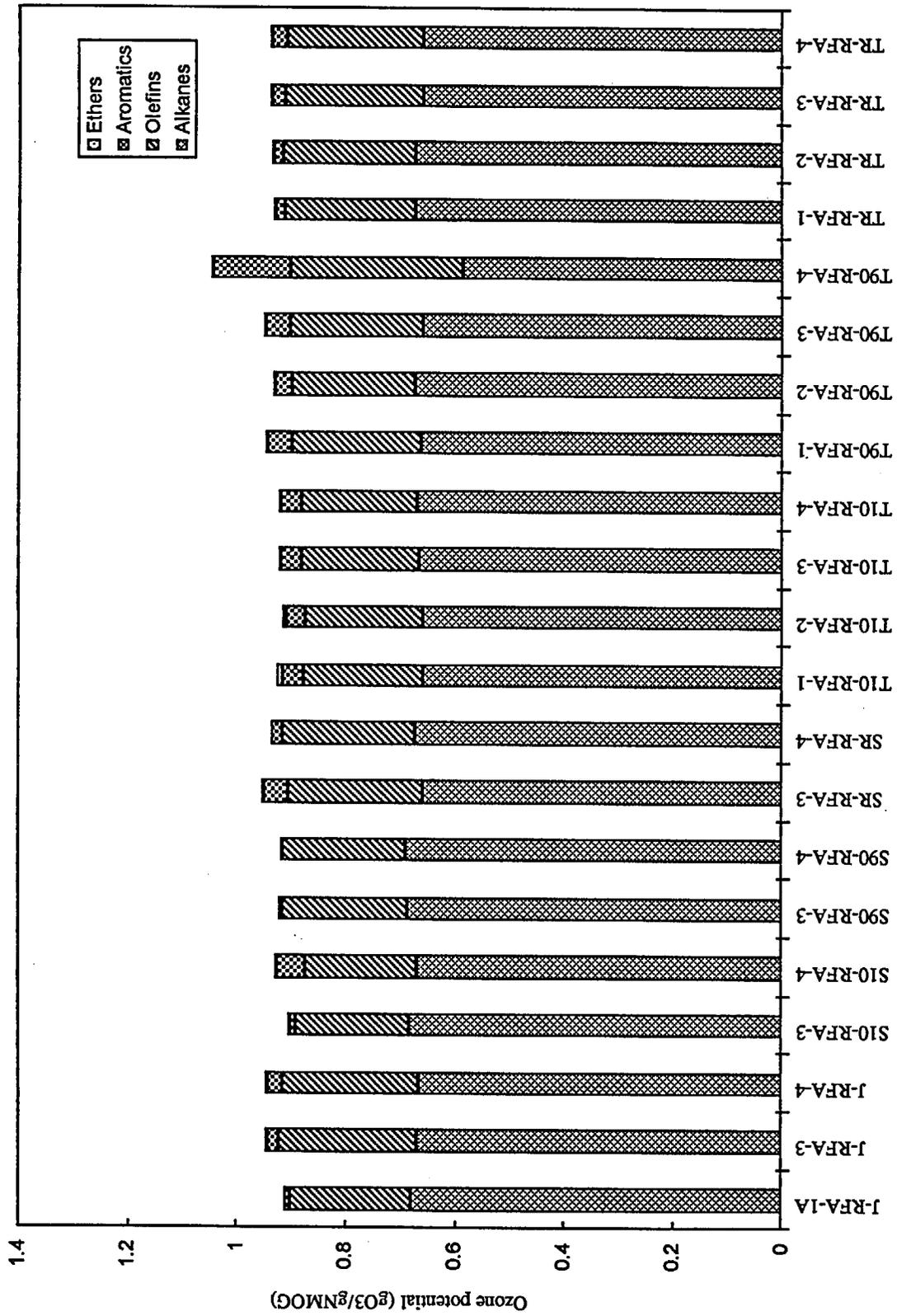


Figure 3-9. Specific MOR reactivity for RF-A

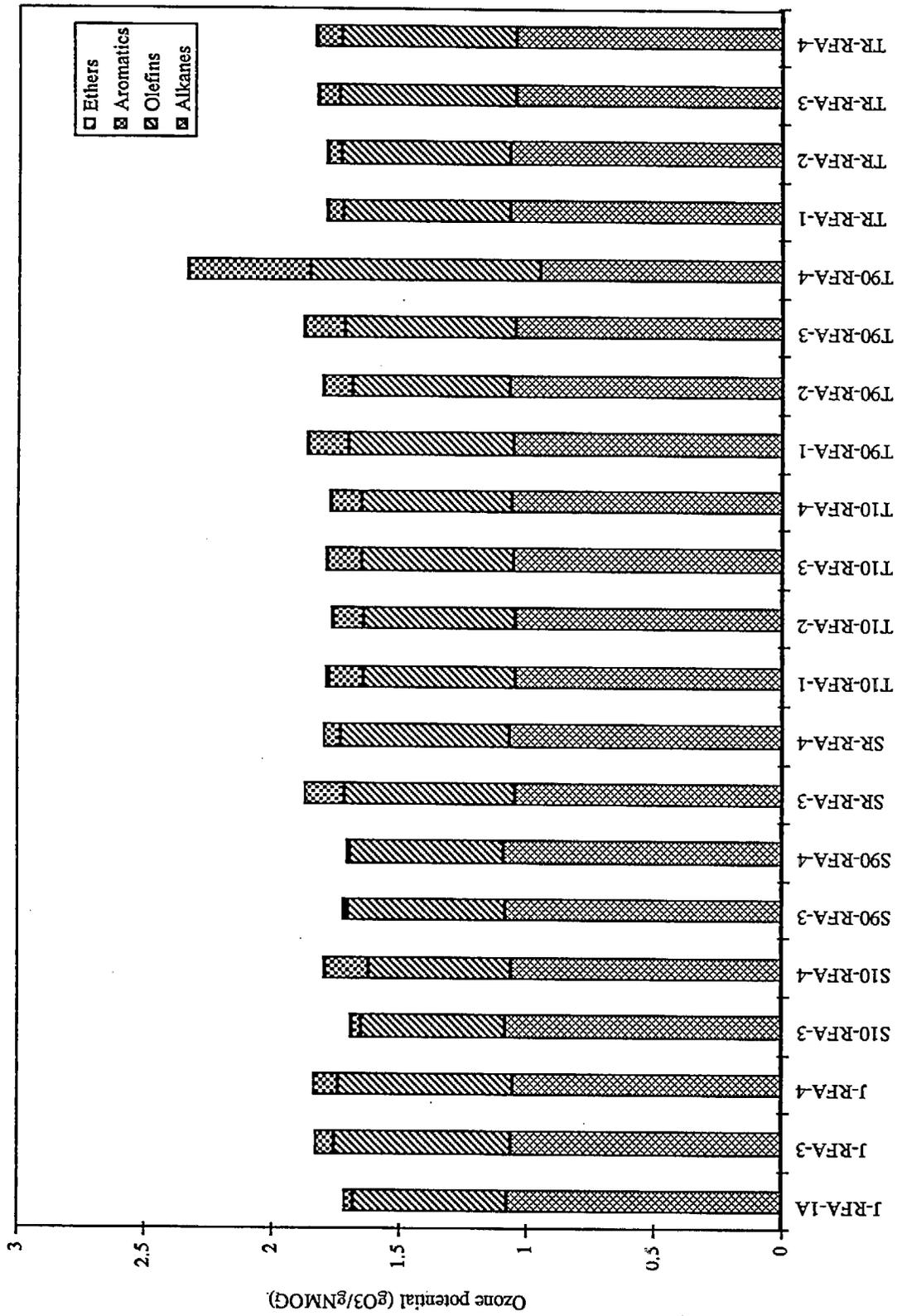


Figure 3-10. Specific MIR reactivity for RF-A

MOR Specific Reactivity (gO₃/gNMOG)

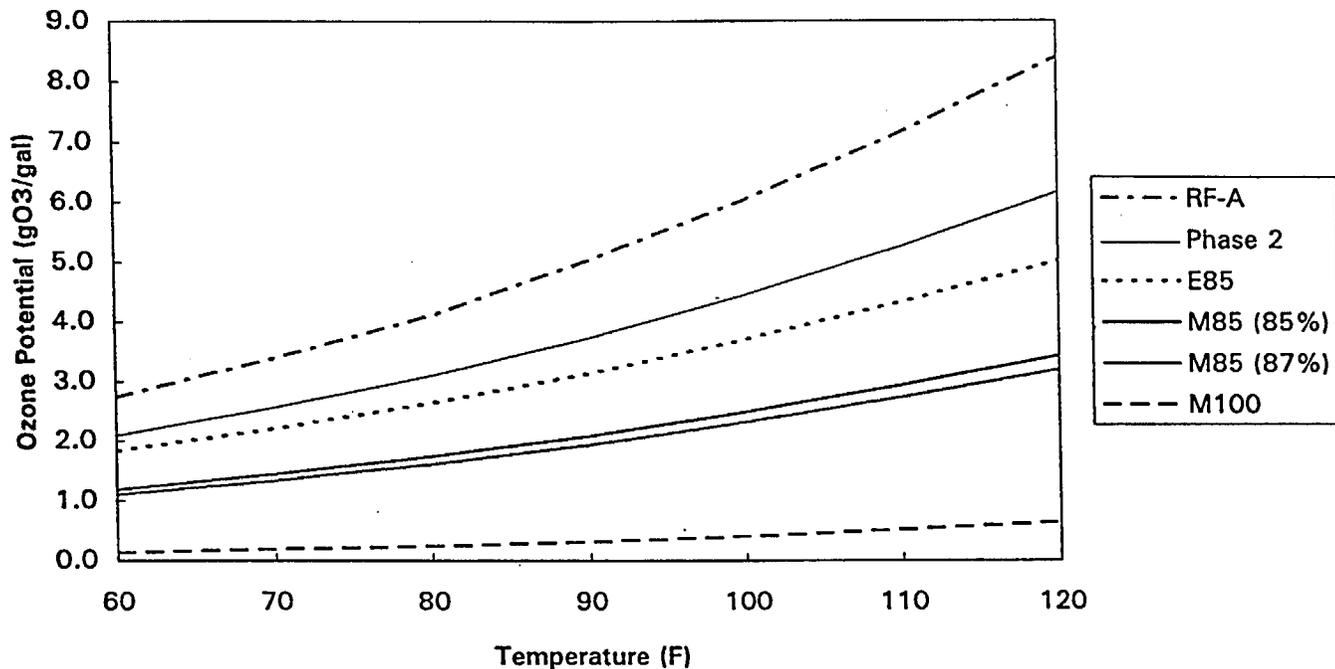
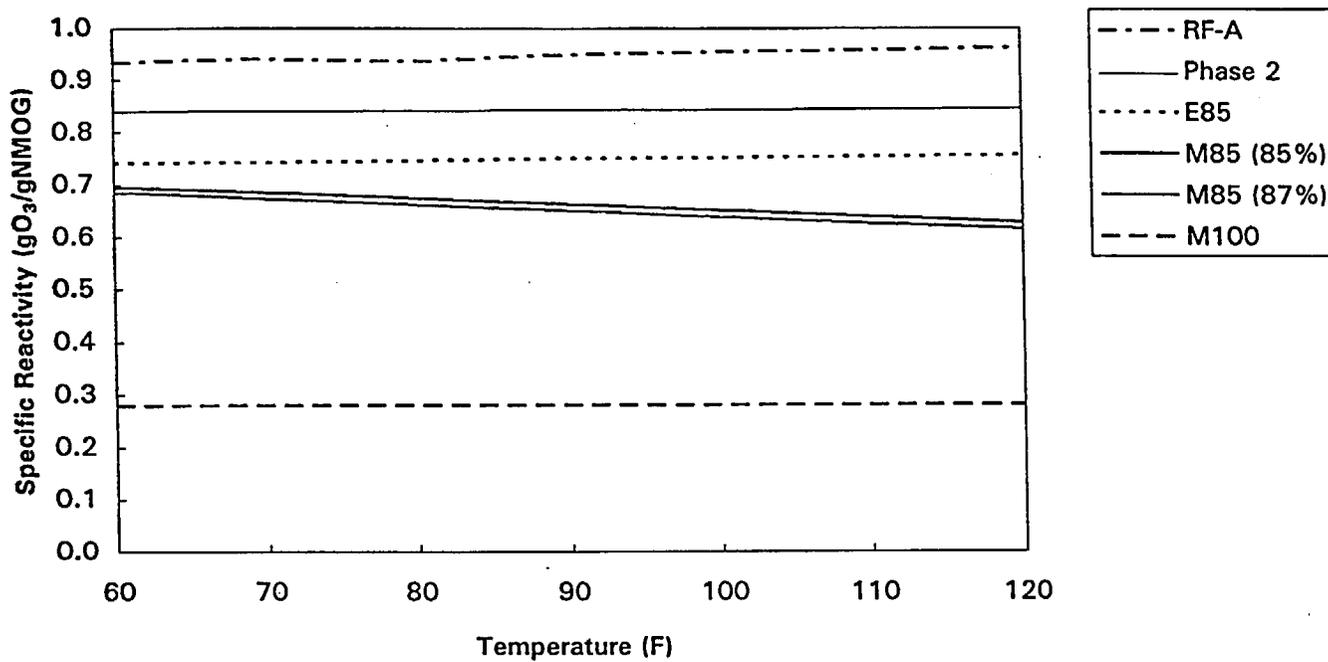


Figure 3-11. Model prediction of ozone potential (MOR)

MIR Specific Reactivity (gO₃/gNMOG)

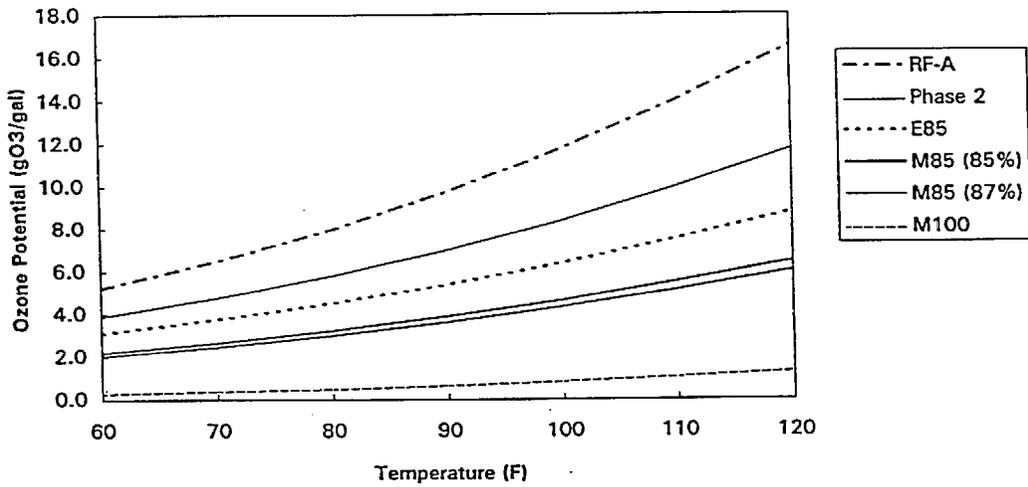
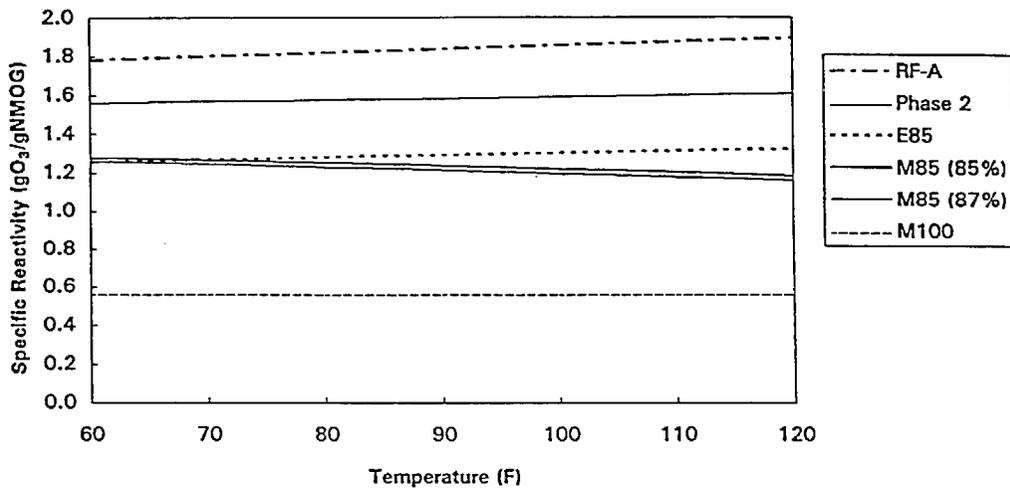


Figure 3-12. Model prediction of ozone potential (MIR)

Table 3-6. Specific reactivity assumptions for liquid fuels and vapors (gO₃/g NMOG)

Fuel	Values Used in This Study Based on ARB Data		MRDC Model @ 80°F	
	MIR	MOR	MIR	MOR
<u>Liquid fuel</u>			The equilibrium model results were based on the liquid speciations	
RFA				
Phase 2	3.115	1.170		
M85	2.421	0.959		
E85	0.786	0.361		
	1.467	0.758		
<u>Fuel vapors</u>				
RFA				
Phase 2	1.81	0.91	1.82	0.93
M85	1.63	0.86	1.57	0.84
E85	1.22	0.65	1.23	0.65
	1.24	0.75	1.28	0.75

were used for M85 and E85. The specific reactivity values for the alcohol blends were less controversial than the values for gasoline. All of the specific reactivity values used in this study are in close agreement with the MRDC model estimates (within 5 percent). The MIR for Phase 2 gasoline has the largest deviation from the model prediction.

Several data sources yielded profiles of speciated hydrocarbons for exhaust emissions, fuels, and evaporative emissions. The speciation of a liquid fuel represents the composition of the vapors that would be emitted from a completely evaporated spill. Vapor profiles refer to the composition of the vapor space in a fuel tank that would be released during vapor transfer operations.

Table 3-7 shows the speciated emissions profiles that were identified as part of this study. The emission profiles for speciations in Table 3-7 were not presented on a consistent basis in the original data sources. Some were total hydrocarbon for a specific process in g/hr while others showed a normalized total mass adding to 100 percent. The specific reactivity presents all of these data on a consistent basis. All of the speciation fractions in the database can also be tracked individually to determine total emissions of particular compounds such as toxics. The data base of specific reactivities and profile numbers used in this study is included in Appendix A.

EPA maintains a data base called SPECIATE that includes speciated emission rates for a variety of industrial processes. Other sources of data included the Auto/Oil studies on vehicle emissions. Even when a fuel composition is known, the composition of vapors that are formed in a storage tank need to be determined. Evaporative emissions from vehicles provide insight into the speciation and reactivity of hydrocarbons from different fuel formulations; however, since the vehicles are equipped with charcoal canisters that may preferentially adsorb some hydrocarbons, vehicle data is not an ideal source for speciated hydrocarbon profiles of fuel tank vapors. Given the limited data

Table 3-7. Specific reactivity for various emission sources (gO₃/g NMOG)

PROFILE	(gO ₃ /gNMOG)		Description	Reference
	MIR	MOR		
3	2.272	0.9116	External Combustion Boiler Natural Gas	ARB
4	2.774	1.161	Boilers, refinery gas	ARB
7	0.41	0.18	Assumed profile for NG turbine exhaust	Profile 1001
9	5.77	2.37	Stationary reciprocating diesel engine ^a	SPECIATE
29	6.094	1.858	Refinery Boiler FCC	ARB
31	1.081	0.6779	Refinery-covered drainage separation pits, fugitive	ARB
35	1.38	0.87	Refinery cooling towers fugitive	ARB
51	2.1	0.7102	Refinery flares - NG	ARB
53	0.8483	0.5038	Refinery catalytic reformer - fugitive emissions	ARB
211	0.7719	0.41	Beer fermentation ethanol production	ARB
217	2.607	1.032	Coke oven blast furnace - process gas	ARB
297	0.919	0.567	Oil evaporation, fixed roof tanks	SPECIATE
305	0.84	0.55	Crude oil evaporation, ship storage	SPECIATE
316	0.9656	0.5956	Refinery pipes, valves & flanges	ARB
321	1.099	0.6231	Refinery pump seals composite	ARB
504	2.182	0.9704	External combustion boilers, distillate or residual	ARB
520	0.314	0.2089	Composite natural gas ^a	ARB
521	0.6514	0.379	Composite LPG ^a	ARB
529	1.019	0.6232	Oil and gas extract pipeline valves & fittings	ARB
530	1.022	0.6241	Oil and gas extraction pumps and seals	ARB
531	1.02	0.624	Oil and gas extraction compressor seals	ARB
532	1.023	0.6244	Oil and gas extraction compressor seals	ARB
535	2.338	1.057	Coal combustion -bituminous fluid bed	ARB
560	2.788	1.124	On-road diesel hot exhaust w/o aldehydes	ARB
561	2.788	1.124	Diesel exhaust with aldehydes	ARB
709	3.054	1.156	Compostite summer gasoline liquid ^a	ARB
710	1.934	0.9998	Compostite summer gasoline vapor ^a	ARB
719	1.532	0.6678	NG IC engine	ARB
760	0.8585	0.5508	Diesel vapor	ARB
816	4.607	1.72	Farm equipment diesel hot exhaust	ARB
817	3.812	1.414	Utility gasoline engine hot exhaust	ARB
1001	0.41	0.18	NG engine exhaust	SPECIATE
1011	0.997	0.609	Oil production fugitives, valves & fittings	SPECIATE
1012	0.89	0.55	NG processing fugitives, vlvs & fittings	SPECIATE
1014	1.88	0.95	Smr blnd gasoline fxd roof vents	SPECIATE
1070	0.61	0.39	Methanol prod. purge vents	SPECIATE
1071	0.62	0.4	Methanol production distillation vent	SPECIATE
1084	1.75	0.77	Biomass boiler exhaust	SPECIATE
1185	2.57	0.96	Coal boiler exhaust	SPECIATE
1190	1.62	0.49	Gasoline marketing vapor ^a	SPECIATE
1207	1.2	0.66	Crude oil drilling water flood of well heads	SPECIATE
2000	0	0	Zero ozone potential	-
8100	2.272	0.9116	Gasifier purge, biomass	Profile 3
8101	2.272	0.9116	Gasifier purge, coal	Profile 3
8102	2.272	0.9116	POX purge vent	Profile 3
8103	2.272	0.9116	NG reformer	Profile 3
8105	2.272	0.9116	LPG combustion	Profile 3

Table 3-7. Specific reactivity for various emission sources (gO₃/g NMOG) (concluded)

PROFILE	(gO ₃ /gNMOG)		Description	Reference
	MIR	MOR		
8200	0.56	0.28	Methanol production and marketing	M100
8203	2.272	0.9116	NG productin and marketing composite	Profile 3
9001	2.64	0.96	Indolene liquid ^a	Furey
9002	1.41	0.79	Indolene vapor ^a	Furey
9003	2.94	1.12	1986 RUL liquid liquid ^a	Furey
9004	1.41	0.082	1986 RUL vapor ^a	Furey
9005	3.22	1.20	RF-A liquid ^a	Auto Oil
9006	2.56	0.86	RF-C liquid ^a	Auto Oil
9007	1.96	0.88	RF-A diurnal evaporative composition ^a	Auto Oil
9008	2.03	0.79	RF-C diurnal evaporative composition ^a	Auto Oil
9009	3.62	1.32	ARCO unreformulated premium ^a	Boekhaus
9010	3.37	1.20	ARCO EC-P gasoline ^a	Boekhaus
9011	3.07	1.16	ARCO Unleade regular gasoline ^a	Boekhaus
9012	2.38	1.04	ARCO EC-1 ^a	Boekhaus
9051	2.06	0.9116	Natural gas flares (No. 51)	SPECIATE
9794	1.63	0.86	Phase 2 storage tank	FC Section 3 ^b
9795	3.42	1.96	RFG Base/TLEV car exhaust, RF-C	Auto Oil
9796	2.421	0.9586	Phase 2 liquid	FC Section 3
9878	1.24	0.745	E85 Storage tank	FC Section 3
9879	1.24	0.745	E85 vapor vehicle	FC Section 3
9880	1.4668	0.7576	E85 liquid	FC Section 3
9950	2.788	1.124	Diesel truck exhaust with aldehydes	ARB 561
9951	3.42	1.96	Gasoline Base/TLEV car exhaust, RF-A	Auto Oil
9974	2.82	1.7	RFG exhaust	Auto Oil
9978	1.22	0.655	M85 vapor, storage tank	FC Section 3
9979	1.22	0.655	M85 vapor vehicle	FC Section 3
9980	0.7856	0.3611	M85 liquid	FC Section 3
9982	1.35	0.054	Diesel liquid estimate	Estimate
9991	0.482	0.311	LPG composition (natural gas derived) ^a	FC Section 3
9989	1.34	0.72	E100 liquid/ vapor	E100
9990	0.56	0.28	M100 liquid/ vapor	M100
9991	0.703	0.401	LPG composition (petroleum derived)	FC Section 3
9992	0.416	0.275	LNG composition	FC Section 3
9993	0.416	0.275	CNG composition	FC Section 3
9994	1.81	0.93	RFA storage tank	FC Section 3
9995	1.81	0.93	RFA vapor vehicle	FC Section 3
9996	3.1149	1.1696	RFA liquid	FC Section 3

^a Interesting profiles not used in this study

SPROF2.XLS

^b Calculated from information in Section 3 of this Study.

on fuel vapor compositions, data for other gasoline formulations are shown in Table 3-7. These data can provide insight into the variability in ozone potential for different fuel formulations.

Gaseous fuels such as CNG and LPG also have low specific reactivities. The specific reactivities of combustion products and crude oil vapors are between those of natural gas and gasoline. Not all of the speciations in Table 3-7 were used in this study (these are indicated with a footnote (a)). They are presented to give the reader a sense for the range in specific reactivities. Examining the specific reactivities in the SPECIATE database suggests that the data quality varies for different profiles. For example, the only NMOG component for natural gas turbine exhaust is formaldehyde (with a balance of methane). Profiles for internal combustion natural gas engines were used instead. Vapors from crude oil storage tanks include no olefins and no heavy aromatics. Similar results are usually presented for natural gas.

Profile 3 was used to represent emissions from natural-gas-fired power plants. More data needs to be evaluated on this emission source given the interest in power generation emissions. A liquid fuel speciation for diesel was unavailable. The specific reactivity of diesel was estimated from a mixture of 60 percent paraffins (dodecane and cycloparaffins), 30 percent aromatics (naphthalene), and 10 percent olefins (nonene).

Figures 3-13 and 3-14 show the range in ozone potential for liquid fuel samples. Several fuel analyses were performed for RF-A and Phase 2 certification fuel by ARB and others. There is little variation in the ozone potential from the two independent samples with three analyses. The ozone potential of RF-A is very close to that of the composite 1987 California fuel developed by Harley¹.

Figures 3-15 and 3-16 show the ozone potential of fuel vapors. Again, the 1987 composite gasoline is close to the median result for RF-A. There was more variation in the ozone potential for vapors since vapors were collected over a range of temperature conditions. Weathering was probably not a factor in the variation since the samples were all collected from a drum with fairly rapid fuel removal. The higher variation in ozone potential from RF-A was probably due to its higher butane content. The fraction of butane in the vapor space varied considerably over the range of fuel temperatures tested. Indolene does not accurately reflect the vapor composition of fuels used in California. The ozone potential of Indolene vapors is considerably lower than those of other gasolines due in part to its low olefin content and also to its higher butane content.

¹ It is so close one might wonder if Harley had access to RF-A. Otherwise, an independent assessment verifies that RF-A represents the ozone potential, if not the sulfur content, of fuels sold in California.

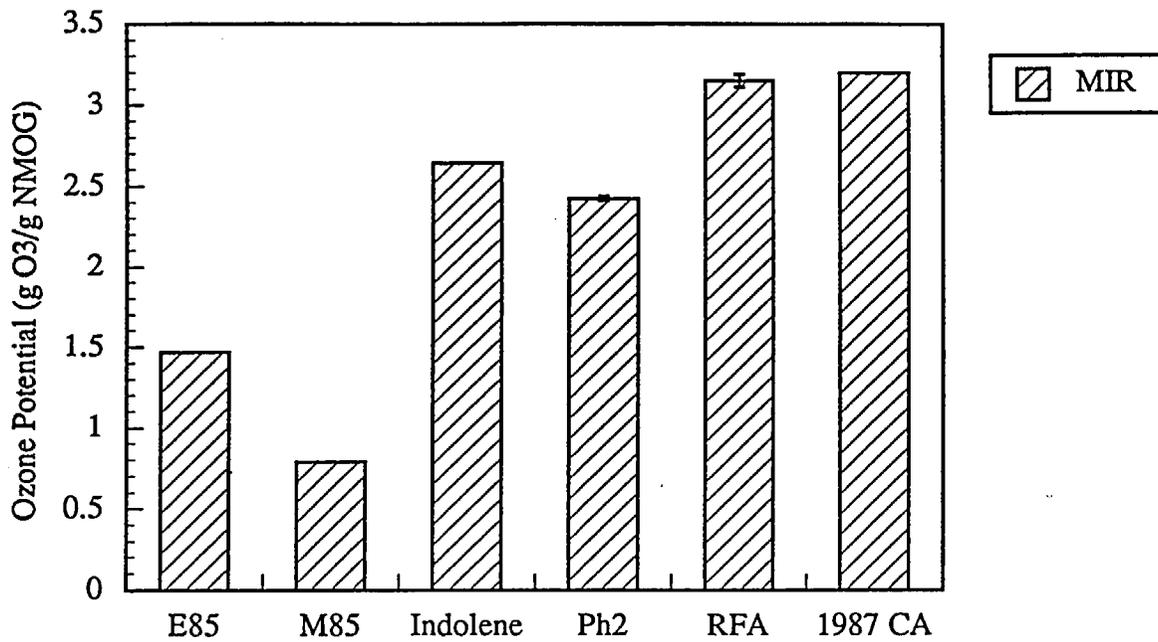


Figure 3-13. Range of specific MIR activities for liquid fuels

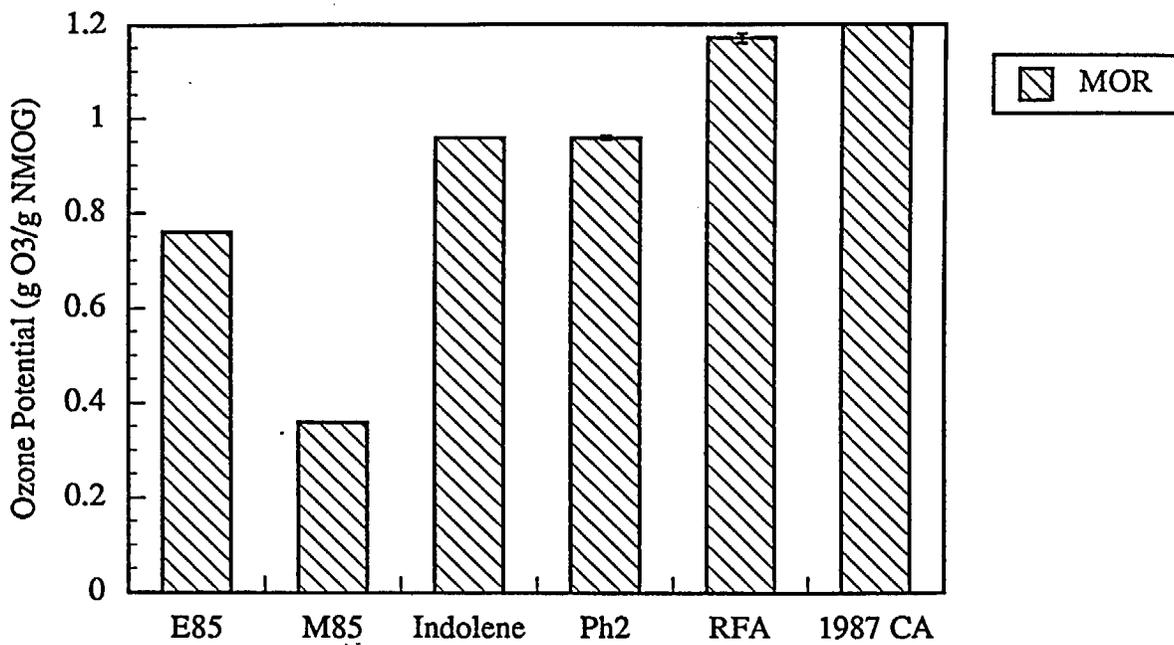


Figure 3-14. Range of specific MOR reactivities for liquid fuels

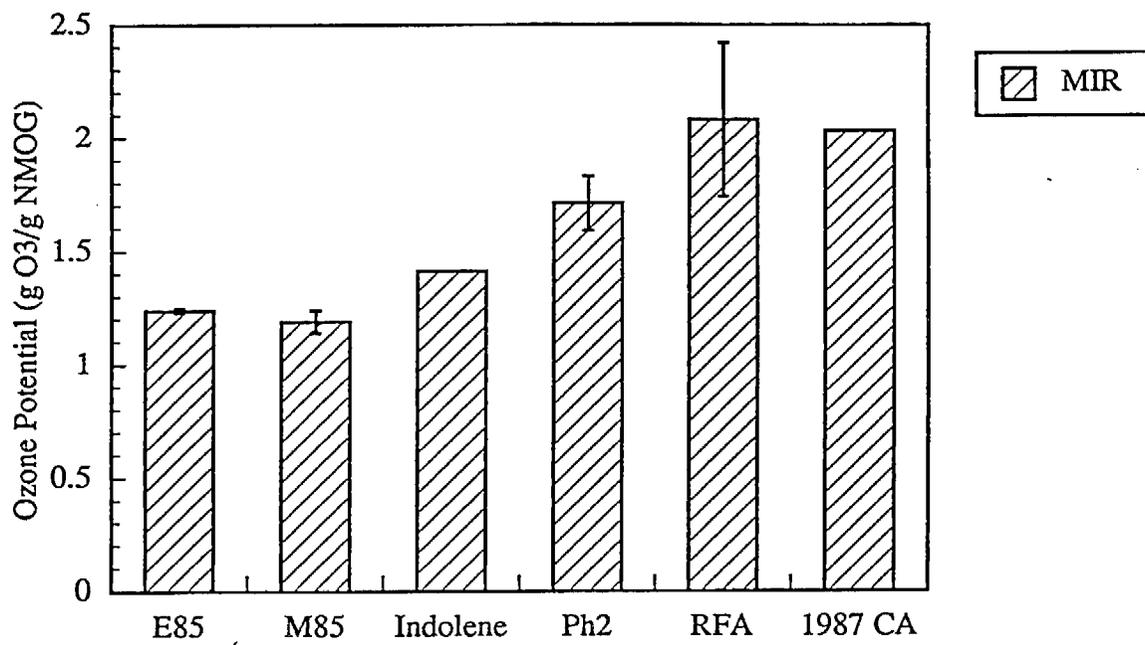


Figure 3-15. Range of specific MIR activities for fuel vapors

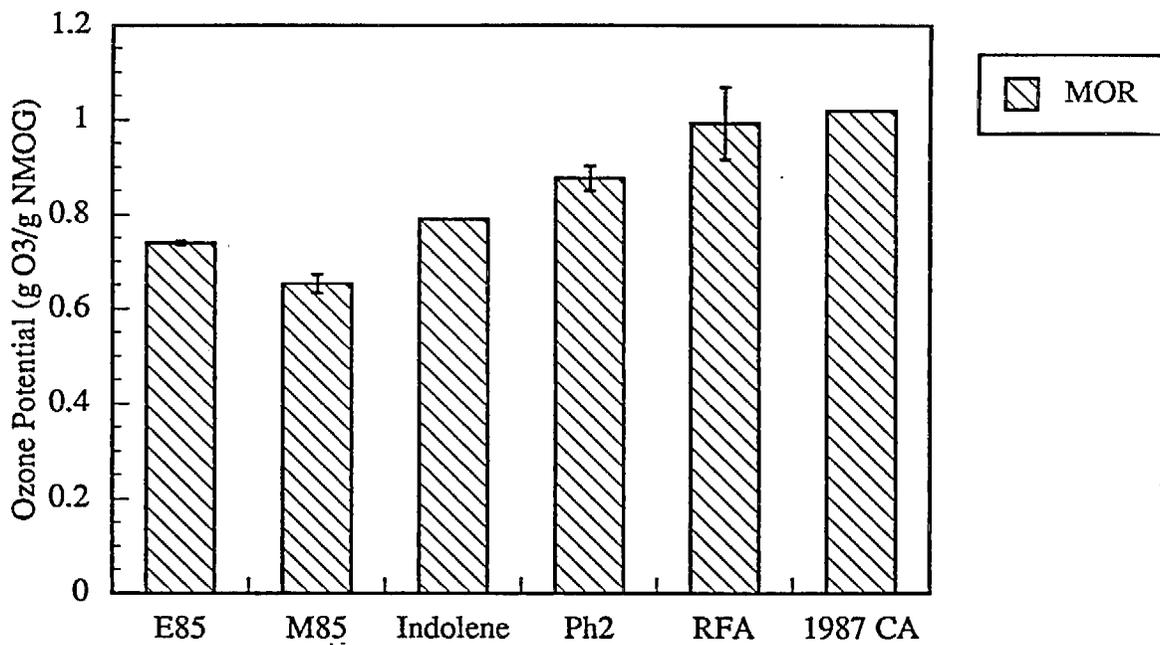


Figure 3-16. Range of specific MOR reactivities for fuel vapors

SECTION 4

DEFINITION OF FUEL CYCLES

This study considered fuel-cycle emissions from 10 vehicle fuels. Many of these fuels can be produced from several feedstocks. The analysis considered an incremental gallon or equivalent fuel unit consumed in the South Coast Air Basin. In order to help evaluate the impact on local emission inventories and air quality as well as considering the differences between local emission rules, the emissions were geographically categorized. Emissions for fuel production in the South Coast Air Basin were also sorted to count sources that correspond to incremental fuel production. Emissions will change with respect to current conditions because of regulatory requirements and will also vary with different production and distribution technologies. Four scenarios, or cases, were developed to cover the range in emissions due to emission assumptions. Table 4-1 shows the fuel/feedstock combinations considered in this study. The codes that correspond to the fuels and feedstocks are used later to identify emission rates in a database. The combination of feedstocks and fuels represents a specific combination of production technologies and feedstocks. Several feedstocks for methanol production are considered separately, while a combination of feedstocks is considered for ethanol, hydrogen, and electricity production. M100 from natural gas is considered separately from M85 from natural gas. Other combinations of feedstocks for M100 were not considered since different fuel production technologies do not significantly influence the emissions in the South Coast Air Basin, the focus of the study.

Table 4-1. Feedstock/fuel combinations considered in this study

Feedstock	Feedstock Code	Fuel	Fuel Code
Crude Oil	o	Gasoline	G
Crude Oil	o	RFG	R
Crude Oil	o	Diesel	D
Crude Oil	o	LPG	P
Natural Gas	n	M85	N
Natural Gas	n	CNG	C
Natural Gas	n	LNG	L
Natural Gas	n	M100	M
Biomass	b	M85	N
Biomass	b	E85	E
Various	n	Hydrogen	H
Various	x	Electricity	J

The fuel-cycle emissions in this study are represented as the weighted average of different production and distribution technologies described in this section. Emissions are categorized into the following groupings:

- Extraction
 - Feedstock extraction
 - Feedstock transport
- Production
 - Refining or processing
- Marketing
 - Site storage
 - Transport to bulk storage
 - Bulk storage
 - Transport to local station
- Distribution
 - Local station distribution

Some fuel/feedstock combinations such as methanol from natural gas were represented separately while ethanol from corn, sugar cane, and biomass were combined to simplify the comparison of fuels in Section 7. The diligent reader can investigate emissions from specific technologies and feedstocks by studying Section 5. The basis for scenarios, mix of feedstocks, as well as production and distribution technologies, is described below.

4.1 SCENARIOS

The scenarios in this study, identified as Scenarios 1 through 4, represent emissions for the years 1992 and 2010. Three scenarios for the year 2010 consider a high and low emission range in technologies and feedstocks.

4.2 GEOGRAPHIC DISTRIBUTION

Because some fuels will be produced outside of California, emissions from the entire fuel-cycle will not directly impact California urban areas. Emissions from fuel production and distribution are tracked according to the following locations:

- Within the South Coast Air Basin
- Within California but outside the South Coast Air Basin
- Within the U.S. but outside of California
- Rest of the World outside the U.S.

Emissions for fuel or feedstock transportation are divided into the four geographic distribution categories. Emissions for ships entering and exiting the San Pedro ports were attributed to the South Coast Air Basin for a portion of the trip. The balance of these emissions were attributed to the rest of the world. Over land transport emissions were allocated proportionally to their transport route. Most over land transportation of feedstocks in the U.S. is by Rail. Class eight trucks deliver fuel for

local distribution. This study is intended to be used to evaluate incremental emissions from fuel production as well as average emissions. The interpretation of what emissions correspond to marginal fuel production depends on factors that are discussed in Section 4.10. The focus on marginal emissions raises questions of transporting emissions into and out of the state. For example, methanol could be sold for vehicle use in the South Coast Air Basin without any production emissions affecting local air quality. Similarly, gasoline is transported to other states from the South Coast Air Basin while the refinery emissions contribute to emission inventories in the South Coast Air Basin. Since hydrocarbons are primarily a local emissions issue with respect to ozone formation, only reactivity weighted in the South Coast Air Basin and California are considered.

4.3 INFORMATION ORGANIZATION

Identifying emissions by spatial location complicates the analysis of fuel-cycle emissions considerably since fuel and feedstock transportation distributes emissions in several of the geographic locations considered in the study. Therefore, the information for this project is organized into a database which calculates spacial emissions, reactivity weighted NMOG (ozone potential) in the South Coast Air Basin, and combines these results with vehicle fuel economy to represent fuel-cycle emissions on a g/mi basis. The information is in four databases which include the following topics:

- Speciation and ozone potential (specific reactivity)
- Production and distribution emission rates
- Emission weighting and spatial distribution
- Vehicle fuel economy

Assumptions for emission scenarios, geographic distribution, production and distribution for the fuel/feedstock combinations, and production and distribution technology mixes are discussed below. Further information on the mix of technologies and energy use parameters is provided in Section 5. These databases are included in Appendix B.

4.4 PETROLEUM FUELS

Gasoline, reformulated gasoline, diesel, and LPG are produced from crude oil. These fuels share the same crude oil feedstock and therefore the same extraction and feedstock distribution paths. LPG, however, can also be produced from natural gas. This is the more common method of LPG production in the U.S. In California, LPG production was 9.4 MMbbl from natural gas liquid plants and 20.6 MMbbl from refinery production, in 1991 (Shremp, 1995). Table 4-2 shows the assumptions for petroleum production. Petroleum fuel production begins with crude oil wells. Crude oil for refineries in the South Coast Air Basin is produced from off-shore and underground wells in the southern coast and San Joaquin Valley. Heavy crude from Kern County represents a large share of this product. Oil is also imported by tanker from Alaska and overseas. This study allocates emissions from fuel production according to the location where the emissions occur.

Section 5.1 discusses the allocation of emissions to the refining operations and feedstock extraction and transport. As discussed in Section 4.10, the allocation of crude oil production and refinery emissions to the South Coast Air Basin depends on whether an incremental gallon of gasoline or the average gallon of gasoline is considered. For most fuel demand scenarios, alternative fuels will displace incremental gasoline, which would be provided through imports. The validity of this

Table 4-2. Petroleum production and distribution from crude oil

Phase	Scenario 1	Scenario 2, 3, 4
	1992	2010
1. Extraction	40% California 10% South Coast Air Basin 45% Alaska 5% Indonesia	32% California 10% South Coast Air Basin 34% Alaska 24% Indonesia
2. Transport	50% ships 50% pipeline	58% ships 42% pipeline
3. Refining ^a	100% South Coast Air Basin, 1990 inventory	100% South Coast Air Basin, 1990 inventory adjusted for control measures
4. Site storage	Refinery tanks	Refinery tanks
5. Transport to bulk storage	Pipeline	Pipeline
6. Bulk storage	Floating roof tanks in SCAQMD inventory	Floating roof tanks in SCAQMD inventory
7. Transport to local station	Tanker trucks	Tanker trucks with low NO _x engines
8. Local station distribution	Underground tanks vapor recovery for gasoline LPG fueling with venting	Underground tanks vapor recovery for gasoline No venting for LPG fueling

^aRefineries in the South Coast Air Basin operate at capacity. See Section 4.8 for a discussion of the treatment of marginal emissions.

argument depends on the rate of alternative fuels penetration as well as the displacement of crude products by oxygenates.

Emissions from oil production in the South Coast Air Basin are expected to reduce over the next 20 years with the following measures (SCAQMD, 1991, Appendix IV-A):

- NO_x controls on refinery fluid catalytic cracking units
- Emission controls on offshore oil production
- Emission controls from refinery flares
- Carbon absorption, refrigeration, and incineration of organic compounds
- Emissions from bulk terminals

In addition, air toxics rules may further limit emissions from oil production, refining, and marketing. The four scenarios incorporate the SCAQMD emission standards into refinery, production and distribution emissions.

Crude oil production techniques depend on the demand for oil. Increased use of more energy intensive techniques such as enhanced oil recovery would correspond to higher petroleum prices. Presumably supplies of readily available oil would be suppressed because of geopolitical considerations or lack of supply. This report does not attempt to predict a change in oil feedstocks or changes in production techniques over the scenarios in this study. However, the trend in California is to extract more oil through thermally enhanced oil recovery (TEOR).

4.4.1 Crude Oil Supplies

California processes about 1.8 million barrels of crude oil per day. In 1992, 50 percent of this oil was produced in California; 45 percent was imported from Alaska; and the remaining 5 percent was imported from foreign sources. Crude oil in California is primarily a heavy variety that is extracted by steam injection. New oil sources in the state are limited and prospects for new off-shore production are unlikely. Figure 4-1 shows California's crude oil production which is expected to continue to decline. California's imports of foreign crude oil have not been large because several refineries have been modified to run efficiently on Alaska North Slope oil (CEC, 1992). CEC projects increased competition for Alaskan oil with an increase in demand in the western U.S. (PADD V) and declining Alaskan Production (Figure 4-2).

For the year 2010, we expect refinery activity in the South Coast Air Basin to remain constant. Monthly crude oil receipts for 1992 are shown in Figure 4-3. By following the trends in

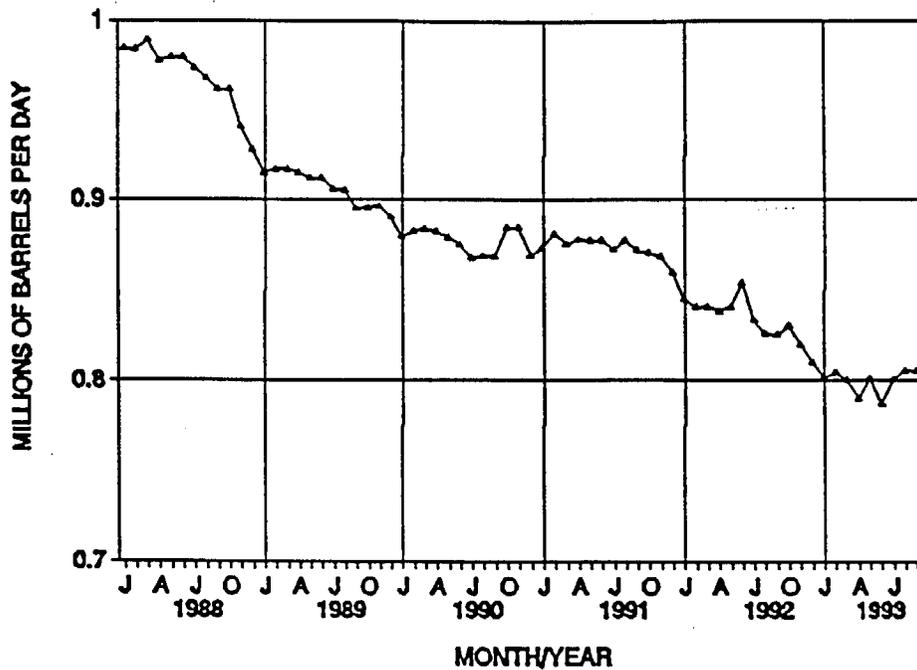


Figure 4-1. California's monthly crude oil production (CEC, 1993)

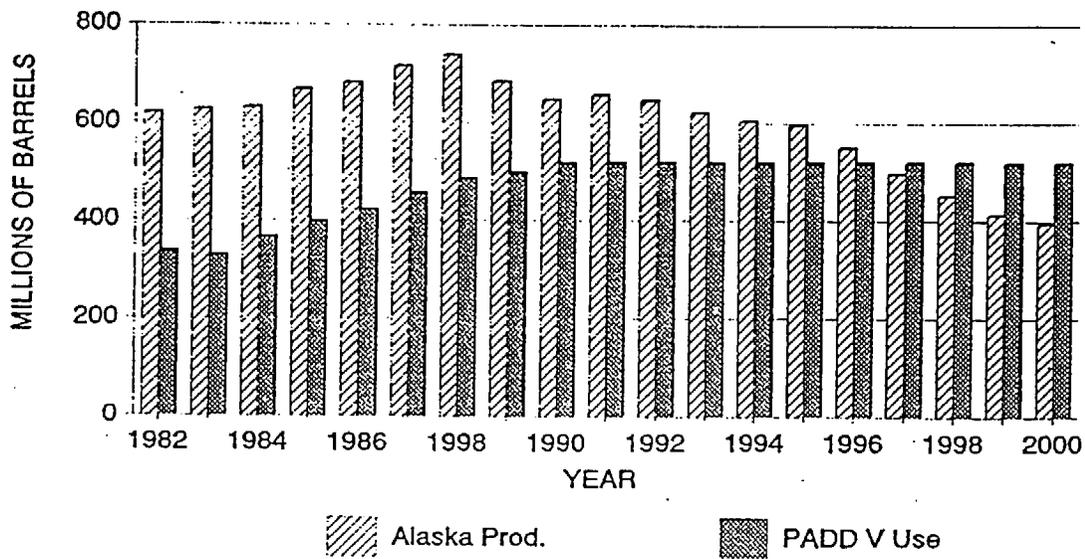


Figure 4-2. Projected Alaskan oil production and PADD V usage (CEC, 1993)

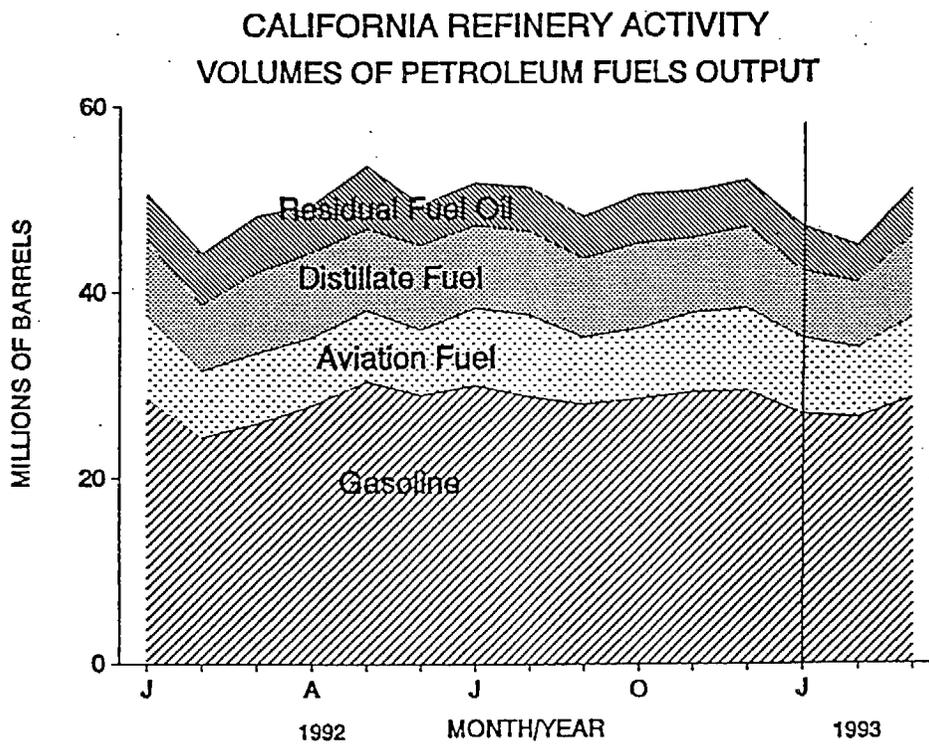


Figure 4-3. Crude oil receipts for California refineries (MMbbl/month)

Figures 4-1 and 4-2, we estimate that California production will drop to 23 million bbl/mo and Alaska imports will drop to 19 million bbl/mo. This mix of imports would result in 42 percent production in California, 34 percent from Alaska, and the remaining 24 percent from foreign imports. This level of imports would maintain current crude consumption with existing refinery capacity. Additional motor vehicle demand could be met with oxygenates, such as MTBE, and alternative fuels. Importing gasoline or increasing refinery capacity are options; however, given the uncertainties in expanding refineries as well as the uncertainty in alternative fuel mix, the prior mix of crude oil imports will be used in Scenarios 2, 3, and 4. Average extraction and processing emissions are allocated in proportion to the location where the crude oil is produced.

4.4.2 Gasoline

Conventional and reformulated gasoline are considered from crude oil. The continued production of conventional gasoline is analyzed through the year 2010. Phase 2 gasoline is formulated to reduce exhaust and evaporative emissions. Light olefins are removed to reduce the reactivity of evaporative emissions. Reducing heavy aromatics improves the reactivity of net exhaust emissions. Benzene is reduced to minimize its direct emissions. This report assumes that the use of MTBE will be used to meet the 2 percent oxygen requirement. Gasoline is distributed with fuel tank truck and service station dispenser vapor recovery.

4.4.3 Diesel

Diesel is distributed in a similar manner as gasoline. Vapor recovery is not required since its vapor pressure is so low. The ARB fuel specification for diesel required low-sulfur and low-aromatics beginning in October 1993. Alternative formulations that meet the ARB requirement appear to represent the majority of diesel sold in California. The production and use of the alternative diesel formulation was assumed for all scenarios.

4.4.4 LPG

LPG is produced as a byproduct of oil refining and is also produced from natural gas production. Oil refineries may burn propane and export butane to the Gulf Coast in the summer. LPG for vehicle use could be diverted from use as a refinery fuel. Comments from one LPG expert suggested that future demand for LPG could be so high that marginal demand must come from natural gas liquids. Given the opportunities for displacing LPG from refinery use, and the source of current LPG, this study assumes refinery-based LPG production. As discussed in Section 5.3, LPG refueling in California must be accomplished with a tank level valve that leaks LPG during the fueling process. This report assumes that California vehicle rules will be changed to allow a no leak system in the year 2010.

4.5 METHANOL

Methanol can be produced from a variety of feedstocks that can generate CO and hydrogen. Most methanol in the world is made from natural gas. One plant in Tennessee makes methanol and other chemicals from coal. Recently there were attempts to convert the Texaco Coolwater gasifier in Dagget, California, to co-produce methanol and electricity from coal and sewage sludge (Air Products). However, this project did not take place. There is also considerable interest in producing methanol from biomass. Work is underway in Hawaii to convert an IGT biomass gasifier to co-

produce methanol. Tables 4-3, 4-4, and 4-5 show the assumptions for methanol production from natural gas, coal, and biomass. Methanol production from coal does not result in different emissions, in the South Coast Air Basin, than methanol production from biomass. Therefore, this feedstock option was not extensively analyzed.

Currently, all of the methanol used in California as a vehicle fuel is produced by steam reforming natural gas. Most of the methanol comes from Canada, with a smaller amount coming from Texas. For the sake of simplicity, transportation from Texas was not considered as this involves rail transport rather than barge transport. Rail transport is more expensive than barge transport for large volumes; therefore, transportation from Texas was not considered. Advances in methanol production technology will result in greater yields. New plants may also be built with combined steam reforming and partial oxidation. The more efficient technologies are reflected in Scenarios 2, 3, and 4. Similarly, for methanol derived from coal and biomass, the more efficient technologies are reflected for the year 2010. Coal is unlikely to be used as a feedstock for methanol production in California because of the high cost of transport; however, petroleum coke is an option for a methanol feedstock.

Fuel distribution for methanol consists of bulk storage terminals and transfer systems similar to those for gasoline. Also, low throughput through the terminals make tank breathing emissions high. Scenarios 2, 3, and 4 reflect higher throughput and improved vapor controls.

Light-duty FFVs currently operate on M85 that meets California specifications. The alcohol content of the blend can vary significantly within this specification. The point along the distribution system at which the gasoline fraction was blended affects total emissions and ozone potential. This includes storing methanol as M100 in a bulk storage terminal and blending the fuel in the tank truck. Storing M85 in the storage terminal was also considered. Storing M85 has the disadvantage of having a higher vapor pressure and reactivity. Furthermore, the product, once blended will no longer be saleable for buses that operate on M100 or for commodity sales such as a feedstock for formaldehyde or MTBE production. The effect of fuel distribution approaches is discussed in Section 5.3. There are two primary methods of blending assumptions for M85, either in the tank truck, or in a bulk tank. Both blending options are considered in the M85 scenarios. For the sake of simplicity, M85 from natural gas is assumed to be blended in the tanker truck, while methanol from biomass is assumed to be blended in a bulk terminal. Since all of the fuel production emissions are outside of the South Coast Air Basin, the biomass and natural gas based feedstock options represent two blending options.

Sufficiently large production volumes were assumed for biomass-based methanol production in California, so that the fuel can be transported to Los Angeles by pipeline. The pipeline options would be much more cost effective than trucking the fuel. The impact on the results of the study are that a bulk storage facility is assumed in Los Angeles, and trucking emissions are the same as those for other liquid fuels.

4.6 ETHANOL

Ethanol is primarily produced from the fermentation of starches that are derived from biomass crops. In the U.S., most ethanol is derived from corn. Corn contains about 65 percent starch with the balance consisting of oil and protein. The oil and protein are sold as byproducts. Most of the starch is converted to ethanol. Sugar beets are another feedstock for ethanol production in the U.S.

Table 4-3. M85 production and distribution from natural gas

Phase	Scenario 1	Scenarios 2, 3, 4
	1992	2010
1. Extraction	100% Canada	50% Canada 50% Indonesia
2. Transport	55% recip. engines 45% gas turbines	50% recip. engines 50% gas turbines
3. Production	100% steam reforming	50% steam reforming 50% part. oxidation
4. Site storage	Canada	Foreign
5. Transport to bulk storage	Tanker ship	Tanker ship
6. Bulk storage	100% S.C. Air Basin M100 internal floating roof tank	100% S.C. Air Basin M100 internal floating roof tank
7. Transport to local station	Tanker truck mixed shipment of M100 and RFG	Tanker truck mixed shipment of M100 and RFG
8. Local station distribution	Underground storage tanks vapor recovery	Underground storage tanks vapor recovery

Table 4-4. M85 production and distribution from coal

Phase	Scenario 1	Scenarios 2, 3, 4
	1992	2010
1. Extraction	100% U.S. mines	100% U.S. mines
2. Transport	Rail	Rail
3. Production	Texaco gasification process	50% Texaco gasification process 50% Shell gasification process
4. Site storage	Utah	Utah
5. Transport to bulk storage	Rail	Rail
6. Bulk storage	South Coast Air Basin internal floating roof tanks	South Coast Air Basin internal floating roof tanks
7. Transport to local station	Tanker truck	Tanker truck
8. Local station distribution	Underground storage tanks	Underground storage tanks

Table 4-5. M85 production and distribution from biomass

Phase	Scenario 1	Scenarios 2, 3, 4
	1992	2010
1. Extraction	California Biomass	California Biomass
2. Transport	Trucks	Trucks
3. Production	IGT gasification	100% adv. gasification
4. Site storage	Sacramento internal floating roof M100 tank	Sacramento internal floating roof M100 tank
5. Transport to bulk storage	M100 pipeline to Los Angeles	M100 pipeline to Los Angeles
6. Bulk storage	Internal floating roof M100 and M85 tank	Internal floating roof M100 and M85 tank
7. Transport to local station	Tanker truck	Tanker truck
8. Local station distribution	Underground storage tanks with vapor recovery	Underground storage tanks with vapor recovery

Overseas producers of ethanol use sugar cane as a feedstock. Since tax advantages for ethanol production favor U.S. producers, most ethanol is expected to come from U.S. corn. Currently, California uses about 60 million gallons of ethanol per year. About 3 million gallons per year are produced from sugar and food wastes in Riverside County.

Advanced technologies are also being developed to produce ethanol from non-starch portions of biomass. This approach will allow a higher yield per ton of biomass and allow the use of biomass feedstocks that do not contain large starch fractions. In these processes, cellulose and ligno-cellulose are hydrolyzed and converted to starches. The starches are then fermented and converted to ethanol. In all fermentation processes, the ethanol is in solution with water and must be separated by distillation or membrane separation.

The scenarios for ethanol production and distribution are shown in Table 4-6. The scenarios for ethanol production reflect different mixes of feedstocks. Improvements in the energy efficiency of corn to ethanol production is reflected in Scenario 2.

Product distribution for ethanol is the same as that for methanol. Current ethanol volume for vehicle fuel in California is small; however, NREL is placing considerable emphasis on ethanol fuel development.

4.7 COMPRESSED NATURAL GAS

Natural gas is available throughout most of California for home heating and industrial energy uses. The infrastructure for the extraction, processing, and distribution of natural gas is available for most potential CNG users where a compression facility might be installed. Figure 4-4 shows the

Table 4-6. E85 production and distribution from biomass, corn, and sugar

Phase	Scenario 1	Scenario 2	Scenarios 3, 4
	1992	2010	2010
1. Extraction	Waste Sugar	Illinois corn	California Biomass
2. Transport	Truck	Truck	Truck
3. Production	Fermentation	Fermentation	SSF ^a
4. Site storage	Riverside, CA	Illinois	Sacramento
5. Transport to bulk storage	None, direct transport to fueling station	Rail	Pipeline
6. Bulk storage	None	Internal floating roof E100 and E85 tank	Internal floating roof E100 and E85 tank
7. Transport to local station	Tanker trucks	Tanker trucks	Tanker trucks
8. Local station distribution	Underground tanks vapor recovery	Underground tanks vapor recovery	Underground tanks vapor recovery

^aSimultaneous saccharification and fermentation of cellulosic biomass.

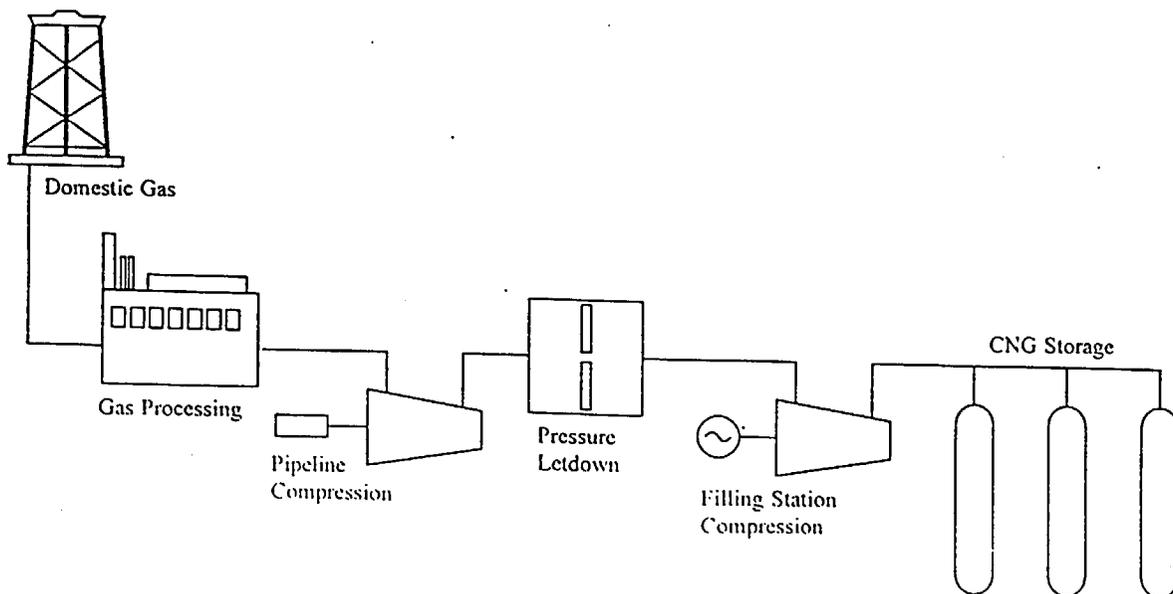


Figure 4-4. Natural gas production and distribution

steps for CNG production. Natural gas is transported in pipelines at 1000 psi and processed in facilities that remove sulfur, water, and capture higher hydrocarbons as byproducts. Natural gas is transported to California in pipelines where it is distributed to the local user. The pressure of the gas at the local user has the most significant impact on the energy required for gas compression. Electric motors power natural gas compressors. Gas is stored in vehicles at 3000 psi pressure. Some buses use higher storage pressures of 3600 psi. Higher storage pressures are also being considered.

Slow fill (or time fill) systems compress the gas and directly fill the vehicle over an extended period of time (usually overnight). The compressor output is only slightly higher than the vehicle storage pressure. Compression is accomplished isothermally since the compressed gas has time to equilibrate with the ambient air temperature.

Fast fill fueling requires slightly more energy. The gas is compressed and stored in a cascade of storage cylinders, or a large capacity compressor produces a flow rate high enough to fill the vehicle in about 10 minutes. The cascade storage pressure or compressor output is about 3600 psi for a 3000-psi vehicle storage system. Also, fast fill fueling results in rapid compression and corresponding temperature rise of the gas in the vehicle. If the vehicle is fueled to 3000 psi, its final fill pressure will drop after the temperature in the vehicle tank equilibrates with ambient air. Sophisticated fueling systems that compensate for the ambient temperature and gas with the vehicle have been designed. Such systems would allow the vehicle to be filled to an effective pressure of 3000 psi. Therefore, after compression to 3600 psi and the fuel heating effect are taken into account, fast fill fueling requires about 22 percent more energy than that of slow fill fueling.

Table 4-7 shows the scenarios for CNG production and distribution. These take into account the expected mix in pipeline compression equipment. Some of the natural gas compressors used for gas transmission may be converted to electric motor; however, the subject of electrification is complex. The existing compressors are subject to emission caps, so there would be limited marginal emissions in the South Coast Air Basin associated with the transmission of additional natural gas for vehicle use. Therefore, the type of transmission equipment would have no impact on the marginal emissions, as discussed in Section 4.12. The extent of conversion to electric compressors was not estimated since it was difficult to quantify and would have had no significant impact on the results of this study.

A mix between fast fill and slow fill service station fueling equipment is also considered. Scenarios 1 and 2 use more compression energy with a higher mix of fast fill while Scenarios 3 and 4 use 70 percent slow fill equipment and assume that 40 percent of fueling stations are connected to higher pressure gas mains.

4.8 LIQUEFIED NATURAL GAS

Table 4-8 shows the assumptions for LNG production and distribution. Extraction and clean up for LNG were considered to be the same as that for CNG. Liquefaction was categorized as Phase 4, site storage. Differences between CNG and LNG production arise from the geographic location of the natural gas supply. Currently, a substantial portion of the LNG supplied in the U.S. is obtained from overseas via LNG tankers.

LNG is produced from natural gas in liquefaction facilities. Natural gas is compressed and cooled and expanded in a multi stage operation. Energy for compression is usually provided with

Table 4-7. CNG production and distribution from natural gas

Phase	Scenario 1	Scenarios 2, 3, 4
	Current 1992	2010
1. Extraction	10% South Coast Air Basin 10% California 60% United States 20% Foreign	50% Canada 50% Texas
2. Transport	55% recip. engines 45% gas turbines	50% recip. engines 50% gas turbines
3. Processing	NG Processing	NG Processing
4. Main Pipeline	55% recip. engines 45% gas turbines	50% recip. engines 50% gas turbines
5. Compressor	55% recip. engines 45% gas turbines	50% recip. engines 50% gas turbines
6. Local pipeline	100% South Coast Air Basin	100% South Coast Air Basin
7. Compressor station	Electric	Electric
8. Local station distribution	Fast and slow fill	Fast and slow fill

Table 4-8. LNG production and distribution from natural gas

Phase	Scenario 1	Scenarios 2, 3, 4
	1992	2010
1. Extraction	Wyoming	50% Canada 50% Texas
2. Transport	55% recip. engines 45% gas turbines	50% recip. engines 50% gas turbines
3. Processing, liquefaction	Wyoming pressure let down liquefier	Bakersfield liquefier
4. Site Storage	No venting	No venting
5. Transport to bulk storage	Storage at site	Storage at site
6. Bulk storage	Storage at site	Storage at site
7. Transport to local station	100% tanker truck with venting	100% tanker truck no venting
8. Local station distribution	100% liquid transfer no venting	100% liquid transfer no venting

natural-gas-powered engines. LNG is stored as a cryogenic liquid in insulated storage vessels. The fuel is generally a liquid at its boiling point. When stored close to atmospheric pressure the LNG temperature is -260°C . LNG tanks allow some heat to enter which boils off some liquid to gas. The pressure in the tank increases and after several days, the gas must be vented. The gas can be vented to the atmosphere recovered as CNG or burned to generate heat. LNG absorbs heat during transfer operations and some liquid is vaporized. Tank truck fuel transfer to a storage facility usually involves passing a small amount of LNG into a heat exchanger to generate gaseous natural gas. This process increases the pressure in the tank truck and forces the liquid into the receiver tank. After transferring the vapors, the gas on the truck is purged.

Figure 4-5 shows several possible modes for LNG production and distribution. Currently, almost all LNG used in vehicle demonstrations has been trucked from Wyoming. Liquefied methane is available from a facility near Sacramento, however, this resource has not been utilized frequently. The LNG from Wyoming is produced in a pressure let-down facility that requires little energy input for liquefaction. For large scale production the liquefier could be at a natural gas peak shaving facility or it could be built as a dedicated facility. It is unlikely that liquefaction facilities will be built in the South Coast Air Basin. The natural gas will more likely be processed nearby. The energy inputs for LNG production will depend on the integration with pipeline pressure requirements. Imported LNG was not considered feasible because of its high ethane content (Pope, 1995). The scenarios for LNG production and distribution reflect differences in energy consumption for liquefaction and assume that LNG emissions from tank truck and vehicle transfer operations will be minimized by the year 2000.

4.9 HYDROGEN

Hydrogen can be produced from the thermochemical processing of carbonaceous materials and the decomposition of water. Most hydrogen today is produced from fossil fuels. Methane, for example, is reformed into CO and hydrogen. The CO is reacted with steam to form additional hydrogen. Non fossil methods of hydrogen reduction include electrolysis of water, thermochemical splitting of water, and photolysis. Electrolysis separates water into hydrogen and oxygen by passing current through an electrochemical cell. The gaseous hydrogen obtained from electrolysis is over 99.9 percent pure, compared to 98 percent purity for fossil-fuel derived hydrogen (Bockris). Conventional electrolysis technology results in efficiencies as high as 82 percent.

Table 4-9 shows the production and distribution scenarios for hydrogen fuel. Currently, few on-road vehicles operate on hydrogen. The University of California, Riverside operates a solar electric hydrogen electrolysis fueling station for experimental hydrogen cars. Therefore, electrolysis was evaluated for Scenario 1. Electrolysis of hydrogen from conventional energy sources was not analyzed since higher hydrogen yields can be obtained from thermochemical processing of fossil fuels, rather than generating electricity first and then generating hydrogen. While the solar electrolysis option is currently not cost effective, several solar hydrogen facilities are being constructed. Some of these facilities use solar energy for compression while others compress the hydrogen with conventional electric power. Analyzing the solar hydrogen option with grid charging provides an interesting comparison of the energy inputs for compressed hydrogen. Scenarios 2, 3, and 4 represent hydrogen production from natural gas and biomass. Another option for hydrogen fueling is on-site reformers that convert methanol (or other energy source) to hydrogen. This alternative was not considered.

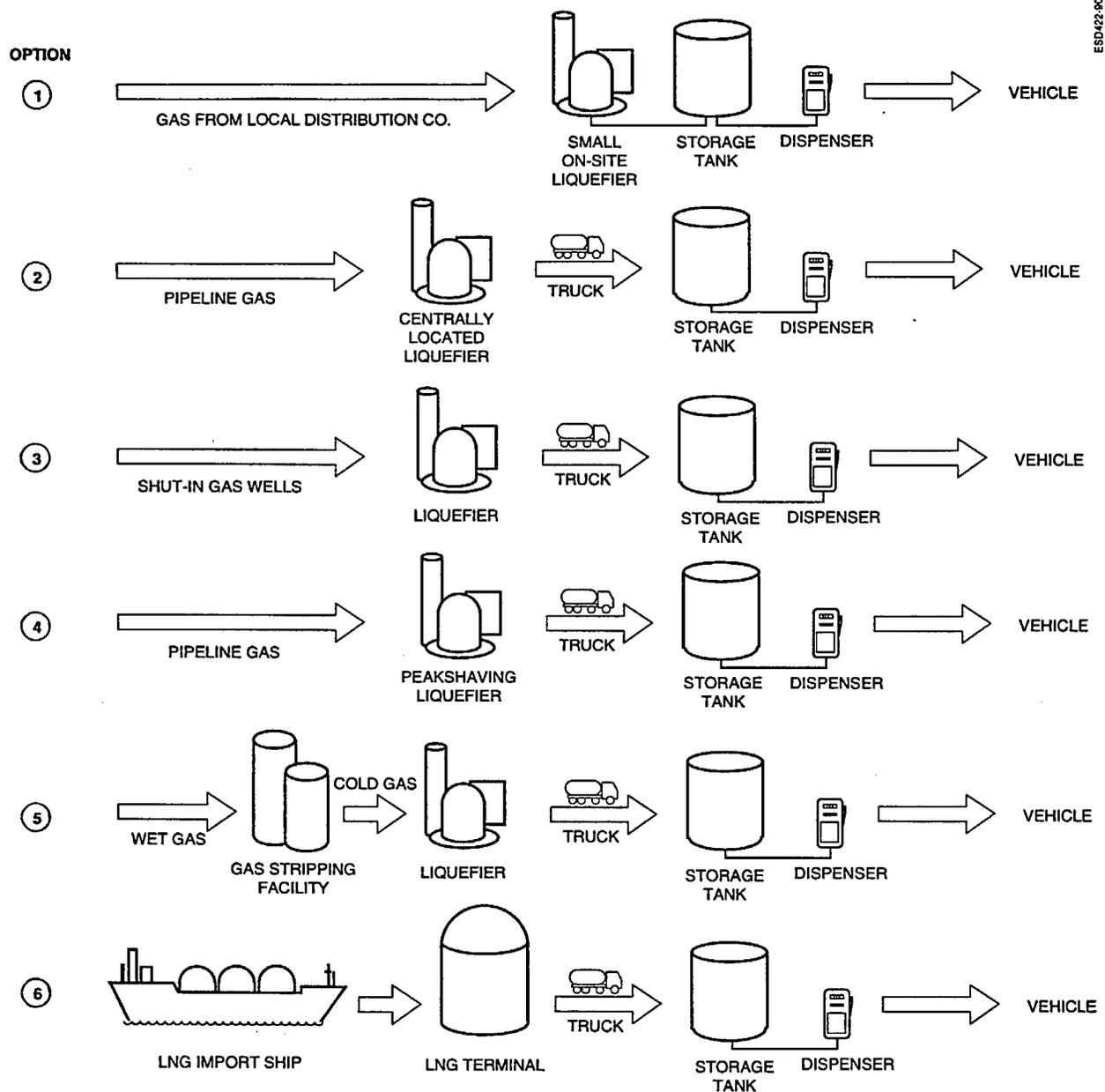


Figure 4-5. Six candidate LNG fuel supply scenarios

Table 4-9. Hydrogen production and distribution from various feedstocks

Phase	Scenario 1	Scenario 2	Scenarios 3, 4
	Current 1992	2010 High	2010 Low
1. Extraction	Solar	CA natural gas	California biomass
2. Transport	—	50% recip. engines 50% gas turbines	Diesel truck
3. Production	—	NG reforming	Biomass gasification
4. Site storage	—	Liquefaction and cryogenic storage	Liquefaction and cryogenic storage
5. Transport to bulk storage	Store and dispense at production facility	Storage at liquefier	Storage at liquefier
6. Bulk storage	Store and dispense at production facility	Storage at liquefier	Store and dispense at production facility
7. Transport to local station	Electric Compression	Truck	Truck
8. Local station distribution	Slow fill compressed H ₂	LH ₂	LH ₂

Distributing hydrogen is difficult because pipelines are not currently available for transporting hydrogen. Existing natural gas pipelines will not be available for hydrogen transport by the year 2010, nor will the hydrogen demand be large enough to support the use of these pipelines. Several compressed hydrogen distribution options are possible. One is storage and dispensing at the hydrogen production facility. This option is only viable for a small vehicle fleet which was the basis for Scenario 1. Other means of distributing compressed hydrogen are possible but were not evaluated further. These include transporting the hydrogen from production facilities to local storage and dispensing stations by tube trailers. Hydrogen is currently available in tube trailers that carry 130,000 scf at 2400 psi. The hydrogen would be compressed to 4000 psi for storage at the vehicle fueling station. This option is currently feasible but not very desirable since the amount of hydrogen energy contained in a trailer is lower than that of other fuels.

Liquid hydrogen (LH₂) is probably the most cost effective means of distributing hydrogen. Hydrogen is liquefied and stored at a bulk distribution terminal. Liquid hydrogen is transported by tank truck and stored as a liquid at a local distribution facility. Vehicle storage can be accomplished with high-pressure storage, liquid, or stored in a solid phase as a metal hydride. Liquid hydrogen can be converted to high-pressure gas or a liquid fuel for vehicles. Liquid storage is used in some experimental vehicles in Germany and is used as the main vehicle option in Scenarios 2 through 4. Boil off from the storage facility and the vehicle need to be managed to minimize hydrogen losses. Metal hydride storage and liquid storage on the vehicle will result in similar fuel-cycle emissions. The main differences will lie in fuel transfer losses and differences in vehicle fuel economy due to a heavier weight with the hydride system. Since hydrogen is not counted as a reactive component, the differences in fuel-cycle emissions between different vehicle storage options were not examined.

4.10 ELECTRICITY

Fuel-cycle emissions for electricity were considered for electric power used in fuel production and distribution, as well as for EV charging. Power generation emissions for electricity production depend on the mix of generation types and fuels (Table 4-10). Transmission losses were considered as part of the power generators.

Power generation from EVs was based on results from the power dispatching model, ELFIN. The model considers the split between daytime and nighttime charging which has a significant impact on emissions.

4.11 ALTERNATIVE FUEL DEMAND AND INCREMENTAL EMISSIONS

The issue of whether incremental or average emissions should be considered brings about spirited discussion among interested parties. The issue is whether to count the emissions from the incremental installed natural gas pipeline compressor or the incremental kWh of electricity generated. Pipeline compression engines in the South Coast Air Basin may be subject to NO_x emission caps and produce no new net emissions. This argument applies to power plants as well. While this is to some extent a philosophical question, the impact on total emissions is significant, and potentially misleading to those who do not read the entire report and only see summaries in newsletters. For example, it can be argued that this gallon is imported into the SCAQMD since refineries currently operate at capacity.

Whether alternative fuels displace an incremental gallon of imported gasoline or gasoline produced in the South Coast Air Basin depends on several factors. Alternative fuels may displace gasoline demand to the extent that the incremental gallon of gasoline used in the basin is not imported. Whether alternative fuels displace an incremental gallon of gasoline depends on the extent of alternative fuel usage and growth in gasoline demand.

Table 4-11 shows a projection for gasoline and alternative fuel demand in the year 2010. The low gasoline/MTBE value is based on ARB's inventory for the South Coast Air Basin. A modest amount of alternative fuel use is added to this value to determine a total fuel demand of 759×10^{12} Btu/yr. The next column projects the gasoline, holding total energy demand constant, while

Table 4-10. Electricity production for EV charging

Phase	Scenario 1	Scenario 2	Scenario 3
	Current 1992	2010 High	2010 Low
1., 2. Extraction and Transportation	Varies with the feedstock. Assumes a weighted average of extraction and transportation emissions for several feedstocks based on CEC's ELFIN model analysis.		
3. Production mix	Average generation	Incremental 80% night 20 % day	Incremental 95% night 5% day

Table 4-11. Projected alternative-fuel demand for the South Coast Air Basin in the year 2010

Fuel Supply	Energy Use (10 ¹² Btu/yr)			Description
	Low	Low	High	
Auto Fuel Demand				Low/Low estimated = ARB inventory value for 2010
Alternative Fuel Supply				Low/High estimate = ARB inventory — alt. fuel projection
Gasoline (HC fraction)	630 ^a	571	720	High/High = 1% more growth — alt. fuel projection
MTBE/Oxygenates	80 ^a	73	91	
<u>Alternative Fuels</u>				
Electricity	18	45	45	Based on EVs displacing 5 to 15 percent of gasoline
Methanol	5	15	15	100,000 vehicles translates into a demand of 10 x 10 ¹² Btu/yr. Range includes 490,000 to 1,150,000 non EV alternative fuel vehicles. Total vehicles in South Coast Air Basin is about 10 million.
Natural Gas	20	35	35	
LPG	1	5	5	
Ethanol	5	15	15	
Hydrogen	0	0	0	Long-term option for LDVs
Total alternative fuels	49	115	115	
Total energy demand for 2010	759	759	926 ^b	High estimate is 1 percent additional growth over 20 years

^a710 x 10¹² Btu/yr = 16,740,000 gal per day of conventional gasoline or 400,000 bbl/d (2010 demand). This fuel demand (in the ARB inventory) corresponds to essentially no growth from 1990 (0.01 percent).

^bHigh estimate is based on 1 percent per year (from 1990 to 2010) compared to the Low Energy Use Scenario.

displacing gasoline with a high alternative fuel use scenario. The net gasoline demand becomes 571 x 10¹² Btu/yr or 320,000 bbl/day. Such a scenario of high alternative fuel use and low growth in demand could result in refineries being shut down; however, exports out of Southern California could make up for the reduction in demand. With little emphasis on increasing fuel economy requirements (CAFE) and slow penetration of alternative fuels, this scenario does not appear likely at this time. When a slightly higher growth in gasoline demand is combined with a high alternative fuel usage, the total gasoline demand continues to grow (to 720 x 10¹² Btu/yr) and in this case alternative fuels would not reduce the output of Southern California refineries.

Alternative fuels can potentially displace 0.4 to 1 million gallons per year (49 to 115 x 10¹² Btu) or up to 18 percent of the gasoline demand in the South Coast Air Basin. Electricity appears to have the strongest statutory requirement for its use as a fuel. National Energy Policy Act and local fleet rule requirements will probably require only a few 100,000 alternative-fueled vehicles which most likely will be natural-gas or alcohol-fueled. LPG may also capture some market share due to its existing infrastructure. Hydrogen is a more long-term option for passenger cars. The first application of hydrogen will probably be in buses. A fleet of 300 hydrogen buses will consume about 1 x 10¹² Btu/yr; however, this value is not counted towards displaced gasoline demand. Some fuel cell powered cars are likely to operate in the year 2010; however, the energy use would round off to zero in Table 4-11. Table 4-11 is based on zero growth in diesel fuel cars (not quantified) which will not affect future gasoline demand. Changes in economic conditions might affect the penetration of alternative fuels. Growth in gasoline demand could be much larger than displacement by alternative fuels. Gasoline demand can be affected by oil prices, fuel taxes, and vehicle fuel economy. The low alternative fuel demand in Table 4-11 corresponds to 4.9 million vehicles including EVs and the high demand corresponds to 11.5 million vehicles including EVs. While 4.9 vehicles may still exceed some projections of alternative fuel use, this value illustrates the effect on gasoline demand. With modest total fuel demand and modest alternative fuel usage, current refinery output levels will be necessary to meet gasoline requirements. However, low growth in total fuel demand and a very high alternative fuel usage will result in an overall reduction in gasoline supply compared to current levels.

The Western States Petroleum Association (WSPA) prepared an analysis of the need to consider marginal emissions. Dr. Greg Nowell¹, of J.T. Nowell and Co., also reviewed the topic and prepared an analysis of the marginal emissions issue. Both are included in Appendix B. The issues of incremental emissions is complex because it affects so many emissions categories. Refinery emissions will not change with new alternative fuel use unless alternative fuel use is far beyond the estimates in Table 4-11. Breathing losses do not depend on throughput, so these emissions might not be counted towards gasoline emissions. However, if fuel station tanks are converted to hold ethanol or methanol, there might be a net reduction in breathing losses per unit of gasoline. Similarly, market pressure from alternative fuels might result in the operation of fewer gasoline tanks.

The allocation of emissions conundrum suggests that the refinery emissions in the South Coast Air Basin are irrelevant and all efforts should be placed on studying emissions from out-of-Basin refineries. This approach was clearly not the intent of the project sponsors. This issue becomes further complicated by existing ethanol plants in the South Coast Air Basin and the fate of permitted emissions if new facilities need to buy offsets or retired facilities sell offsets. Estimating the emissions from South Coast Air Basin refineries and then allocating these emissions to outside California is not meaningful. Therefore, this study presents marginal and average emissions when discussing emissions in the South Coast Air Basin and average emissions when considering global emissions impact.

Therefore, the following approach will be taken:

- Estimate emissions based on average production mix, except for EVs where emissions models exist for EV power consumption

¹ Dr. Nowell is a Professor of Political Science at State University of New York, Albany.

- When comparing emissions in the South Coast Air Basin, determine marginal emissions considering continued refinery operation, emission caps in the South Coast Air Basin, and fuel transport and distribution emissions

A similar issue applies to ozone potential from emissions outside of the South Coast Air Basin. While the oil industry disputes the use of reactivity factors, their use in air quality policy documents is widespread. The Auto/Oil publications also place considerable time evaluating the ozone potential of evaporative emissions. Concerns regarding the use of ozone potential factors include the following:

- The validity of the ozone potential approach is considered unsound by WSPA
- Reactivity factors were developed for stationary emissions, applied to vehicle exhaust and to some extent evaporative emissions. The spatial distribution of emissions varies between vehicle exhaust and evaporative emissions, continuous production facility operation and round the clock gasoline marketing. Reactivity factors are not necessarily applicable outside of the South Coast Air Basin or California, since their relevance depends on background smog formation conditions.

4.12 SUMMARY OF EMISSION ASSUMPTIONS

In order to span the range of uncertainties in the study, a range of assumptions is considered for some parameters. The key parameters that are varied in the different scenarios are shown in Table 4-12. Fuel economy is one of the most important parameters in evaluating fuel cycle emissions. For a given type of vehicle, fuel economy is assumed to be proportional for all vehicle types except for electric vehicles where the consumer may accept some trade offs in vehicle size for extended range. Energy inputs for alternative fuel production are varied among the four scenarios. Fuel spillage assumptions during vehicle fueling are also varied. Section 5 identifies the emission rates and energy inputs for producing and distributing fuels that correspond to Table 4-12. Sensitivity analyses that consider the effect of ambient temperature on fueling emissions and ozone potential is significant but was not performed. The effect of fuel weathering was also not considered in a sensitivity analysis.

Table 4-12. Key fuel-cycle emission assumptions

Category	Emission Source	Assumption
Methanol, crude oil	Shipping distances	Corresponds to distances and feedstock sources in Section 4.
Oil production	Production and refining	For Scenarios 2, 3, & 4. Combustion NO_x = 21% of 1990 SCAQMD inventory. Production and refinery fugitives = 53% of 1990 inventory.
Liquid fuel bulk storage in CA	Phase 4 and 6 storage emissions	Emissions based on tank throughput and formula for tank venting.
Liquid fuel bulk storage outside CA	Phase 4 and 6 storage emissions	Scenario 1 emissions based on tank throughput calculations. For Scenarios 2 & 3, methanol and ethanol throughputs per tank increased to match gasoline. Vapor emissions reduced ($\times 0.53$) for M100, M85, E100, E85, gasoline, and RFG. Reduced ($\times 0.10$) for Scenario 4.
Ethanol from biomass	Process energy input	Feedstocks are waste sugar, corn, biomass, and biomass for Scenarios 1, 2, 3, and 4, respectively. Energy input and locations for processing are: 35,000 Btu/gal natural gas in Riverside for Scenario 1, 35,000 Btu/gal coal for Scenario 2. 36,400 Btu biomass/gal biomass for Scenarios 3 and 4.
Methanol from biomass	Process energy input	Energy inputs are 123,000 Btu biomass and 0.77 kWh electricity for Scenario 1. 100,000 Btu biomass and 1.07 kWh electricity for Scenarios 2, 3, and 4.
Methanol from natural gas	Processing energy input	32,000 Btu/gal reforming Scenario 1, 30,000 Btu/gal for Scenarios 2, 3, and 4.
LNG liquefaction	Liquefaction energy	Pressure let down facility in Scenario 1, 0.4 kWh electricity input. IC engine driven liquefier for Scenarios 2, 3, & 4. 20%, 15%, and 15%, of LNG as natural gas energy input, respectively.
All internal combustion engine vehicles	Baseline vehicle fuel economy	23 mpg for Scenario 1. 27.5 mpg for Scenario 2 & 3. 32 mpg for Scenario 4.
Alternative fuels with internal combustion engines	Fuel efficiency relative to baseline gasoline	Actual 1990 performance for Scenario 1. Slightly higher than gasoline for Scenario 2 and 3. For Scenario 4, M85, E85, CNG, LPG, LNG 5 % higher than gasoline. M100, E100 10 % higher than gasoline.
Hydrogen vehicles	Fuel efficiency	IC engine for Scenario 1. Fuel cell powered with 100% improvement in efficiency for Scenarios 2, 3, and 4.
Electric vehicles	Fuel consumption	0.35 kWh/mi mpg for Scenario 1. 0.25 kWh/mi for Scenarios 2 & 3. 0.2 kWh/mi for Scenario 4.

Table 4-12. Key fuel-cycle emission assumptions (concluded)

Category	Emission Source	Assumption
All liquid fuels, LNG, and LH ₂	Tank truck emissions	Low NO _x engines in 2010 consistent with 2 g/bhp-hr.
All liquid fuels	Fueling spillage	Scenario 3 = 60% of Scenarios 1 & 2, Scenario 4 = 44% of Scenarios 1 & 2.
All liquid fuels	Service station vapor losses	Scenario 4 = 80% of Scenarios 1, 2, & 3 to reflect variation in breathing losses and defect rate.
Hydrogen production	Production and liquefaction	Solar hydrogen with electric compression in Scenario 1. Natural gas reformer with IC engine liquefier in Scenario 2. Biomass gasifier with natural gas IC engine liquefier in Scenarios 3 and 4.
CNG compression	Compression energy	1.2 kWh/100 scf for Scenarios 1 & 2, 1.0 kWh/100 scf for Scenarios 3 & 4.
LPG and LNG venting	Venting emissions	Scenario 1: LPG fueling with outage valve on vehicle and tank truck. Venting of LNG Tank truck at fueling station. Spillage losses correspond to measured volumes in fittings. Spillage from LNG and LPG tank truck hose. Scenarios 2, 3, & 4. EPA VOC rules will eliminate outage valve and tank truck venting losses. Eliminate major tank truck hose spillage.
CNG fueling	Venting emissions	Estimate venting from compressors. Calculate venting losses from CNG fitting. Assume less CNG venting for Scenarios 2, 3, & 4 (80, 60, and 40 percent of Scenario 1) based on requirements for VOC control from fuel stations.
Electric vehicles	Average power plant emissions based on CEC ELFIN model	Average (yr 2000) power plant emissions for Scenario 1 Incremental (yr 2010) 80/20 charging profile emissions for Scenario 2. Incremental (yr 2010) 95/5 charging profile emissions for Scenarios 3 & 4.