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**United States Patent** [19][11] **Patent Number:** **5,653,866**

Jessup et al.

[45] **Date of Patent:** **Aug. 5, 1997**[54] **GASOLINE FUEL**[75] Inventors: **Peter J. Jessup; Michael C. Croudace**,  
both of Santa Ana, Calif.[73] Assignee: **Union Oil Company of California, El**  
**Segundo, Calif.**

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5593,567, which is a continuation of Ser. No. 77,243, Jun.  
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**208/18; 123/1 A; 585/14**[58] **Field of Search** ..... **123/1 A; 208/146,**  
**208/14-18; 585/14**[56] **References Cited****U.S. PATENT DOCUMENTS**

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By controlling one or more properties of a gasoline fuel  
suitable for combustion in automobiles, the emissions of  
NO<sub>x</sub>, CO and/or hydrocarbons can be reduced The pre-  
ferred fuel for reducing all three such emissions has a Reid  
Vapor Pressure no greater than 7.5 psi (0.5 l atm), essentially  
zero olefins, and a 50% D-86 Distillation Point greater than  
about 180° F. (82° C.) but less than 205° F. (96.1° C.)

58 Claims, 9 Drawing Sheets

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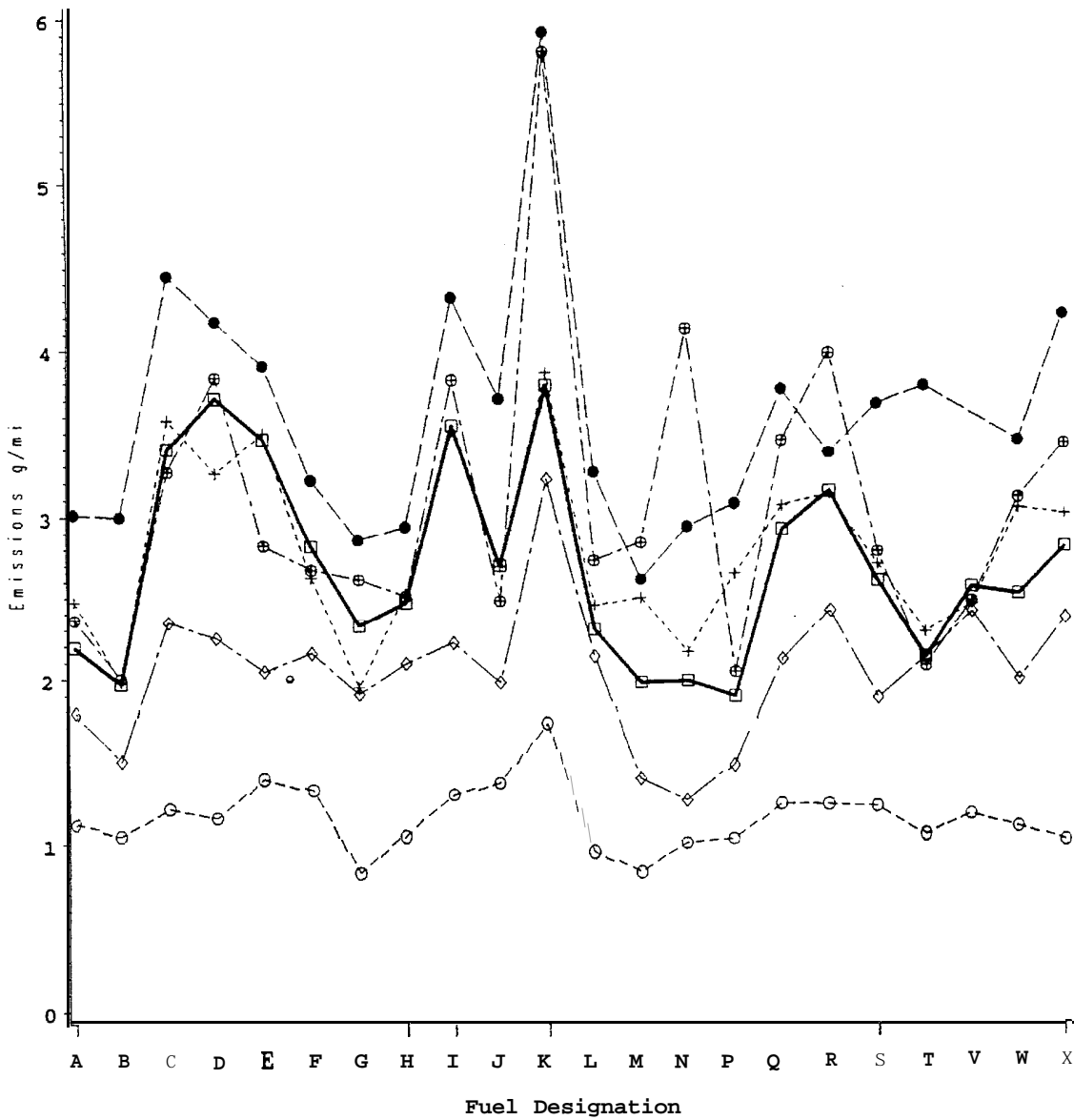
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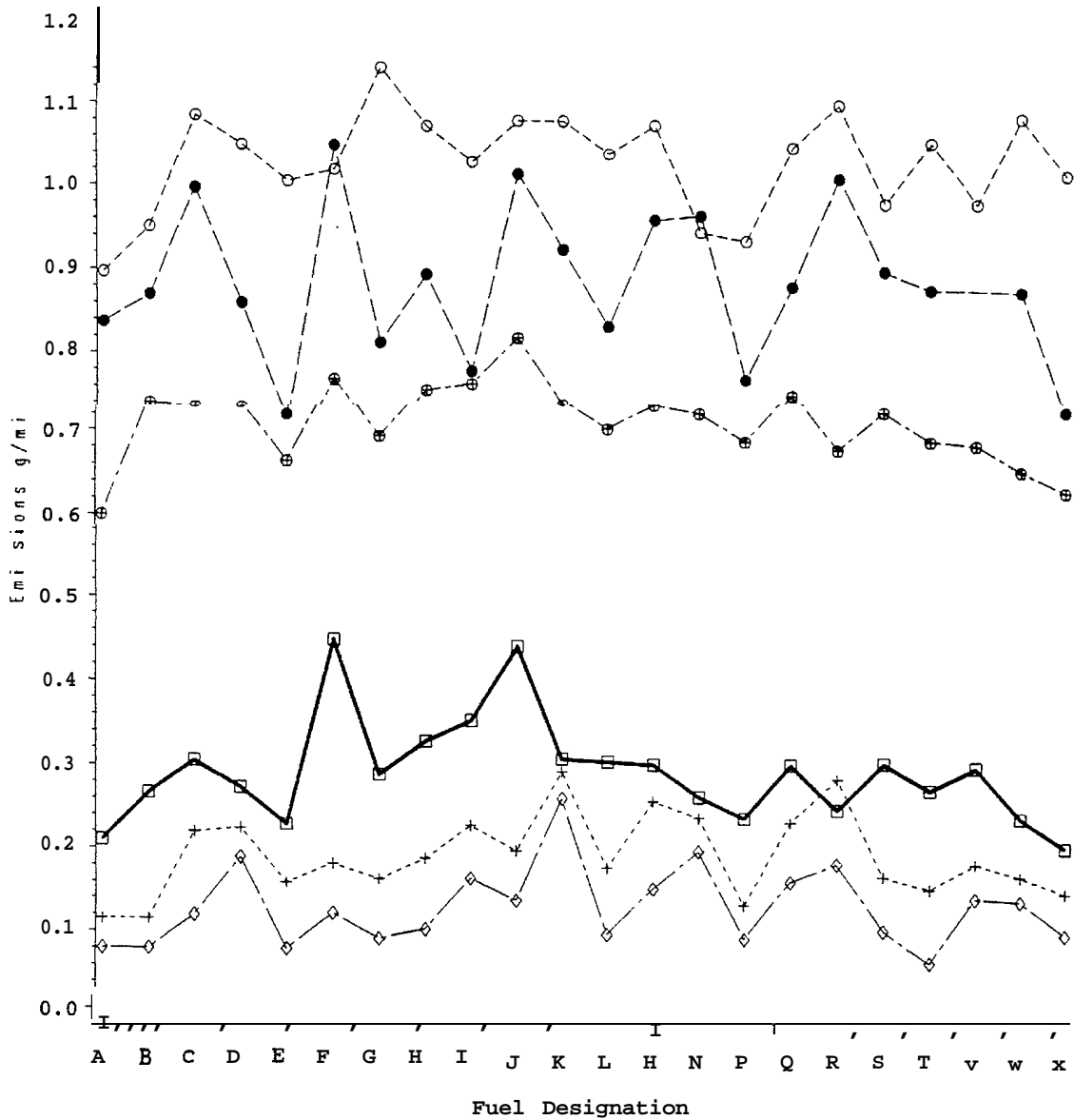


Figure 1  
Emissions Test Data - CO



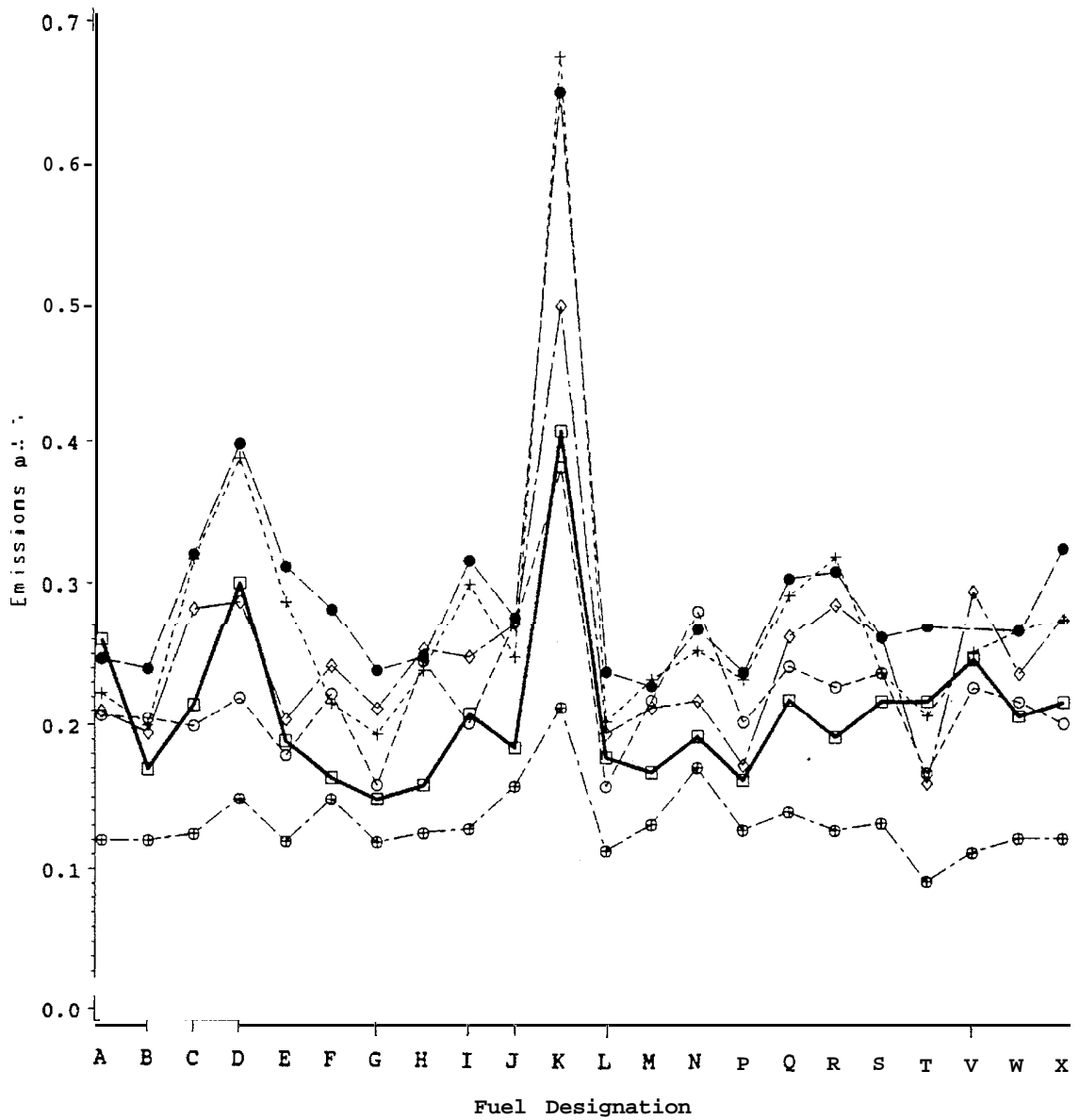
+ + + 1989 Calais    □ □ □ 1988 Olds 98  
o o o 1990 Lincoln    ... 1999 Taurus  
⊕ ⊕ ⊕ 1990 Shadow    ◇ ◇ ◇ 1990 Camry

Figure 2  
Emissions Test Data - NOx



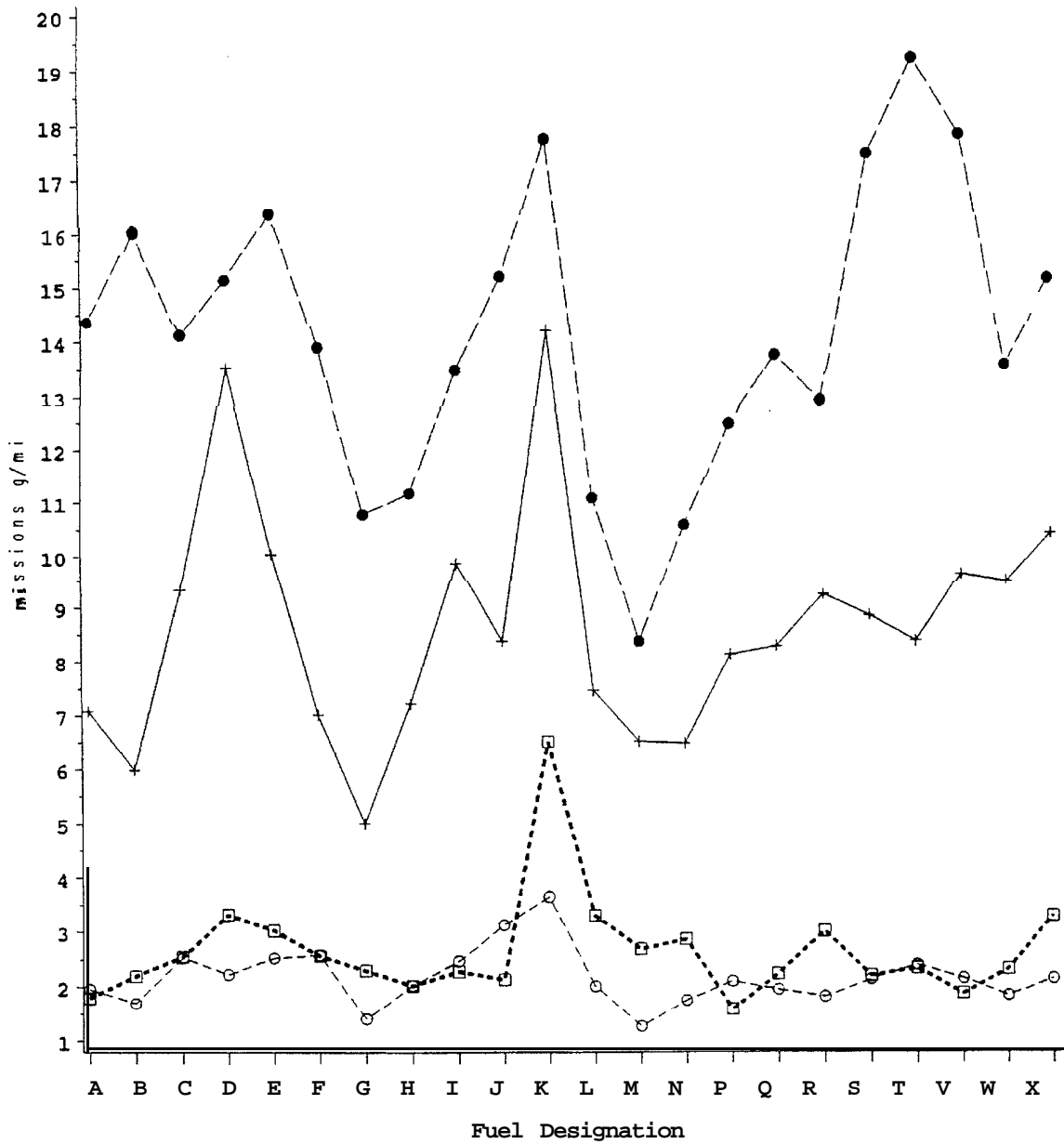
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 ⊕ ⊕ ⊕ 1990 Shadow    ◇ ◇ ◇ 1990 Camry

Figure 3  
Emissions Test Data - HC



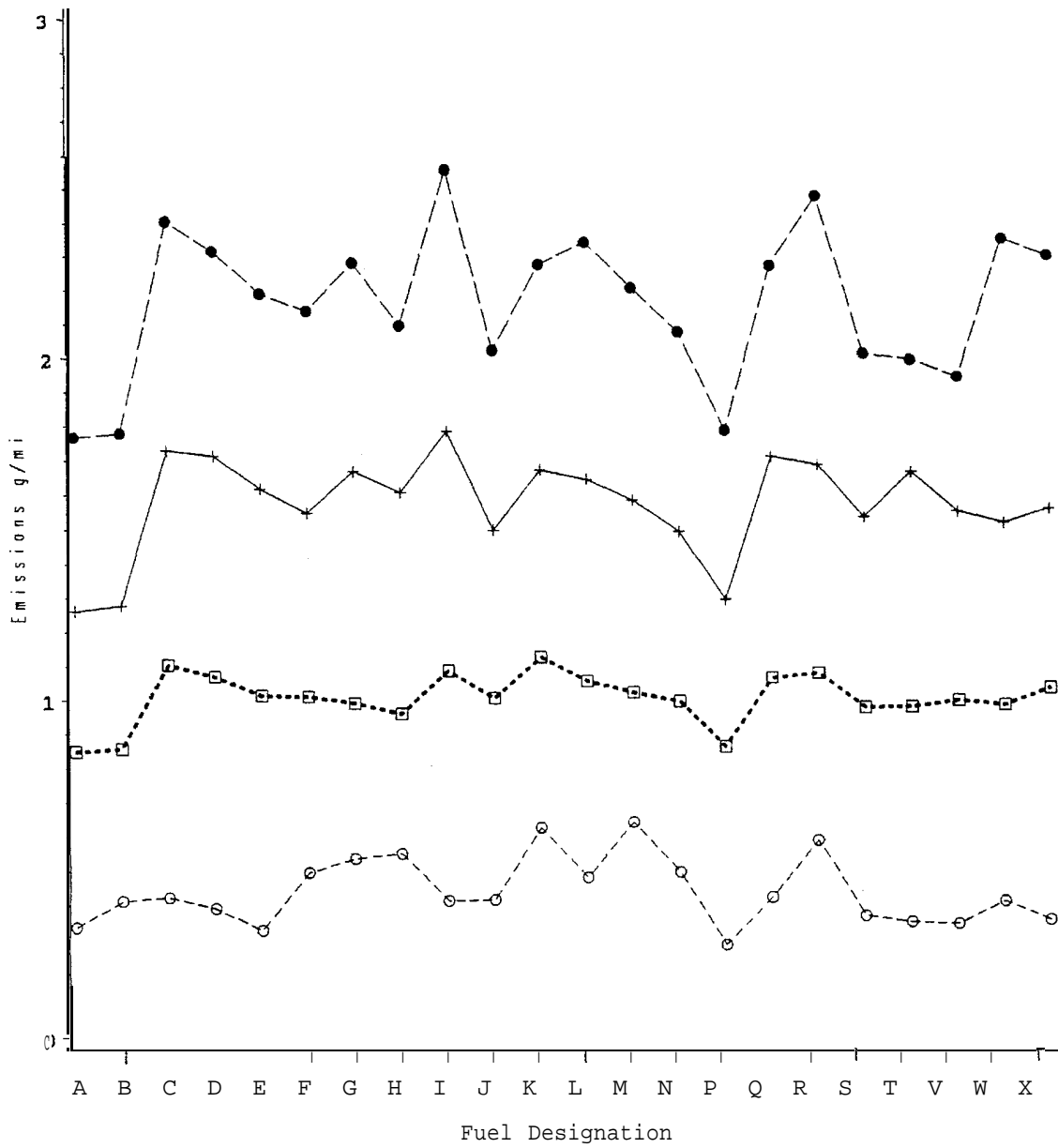
+ + + 1999 Calais    □ □ □ 1999 Olds 99  
○ ○ ○ 1990 Lincoln    ● ● ● 1999 Taurus  
⊕ ⊕ ⊕ 1990 Shadow    ◇ ◇ ◇ 1990 Camry

Figure 4  
Emissions Test Data • CO



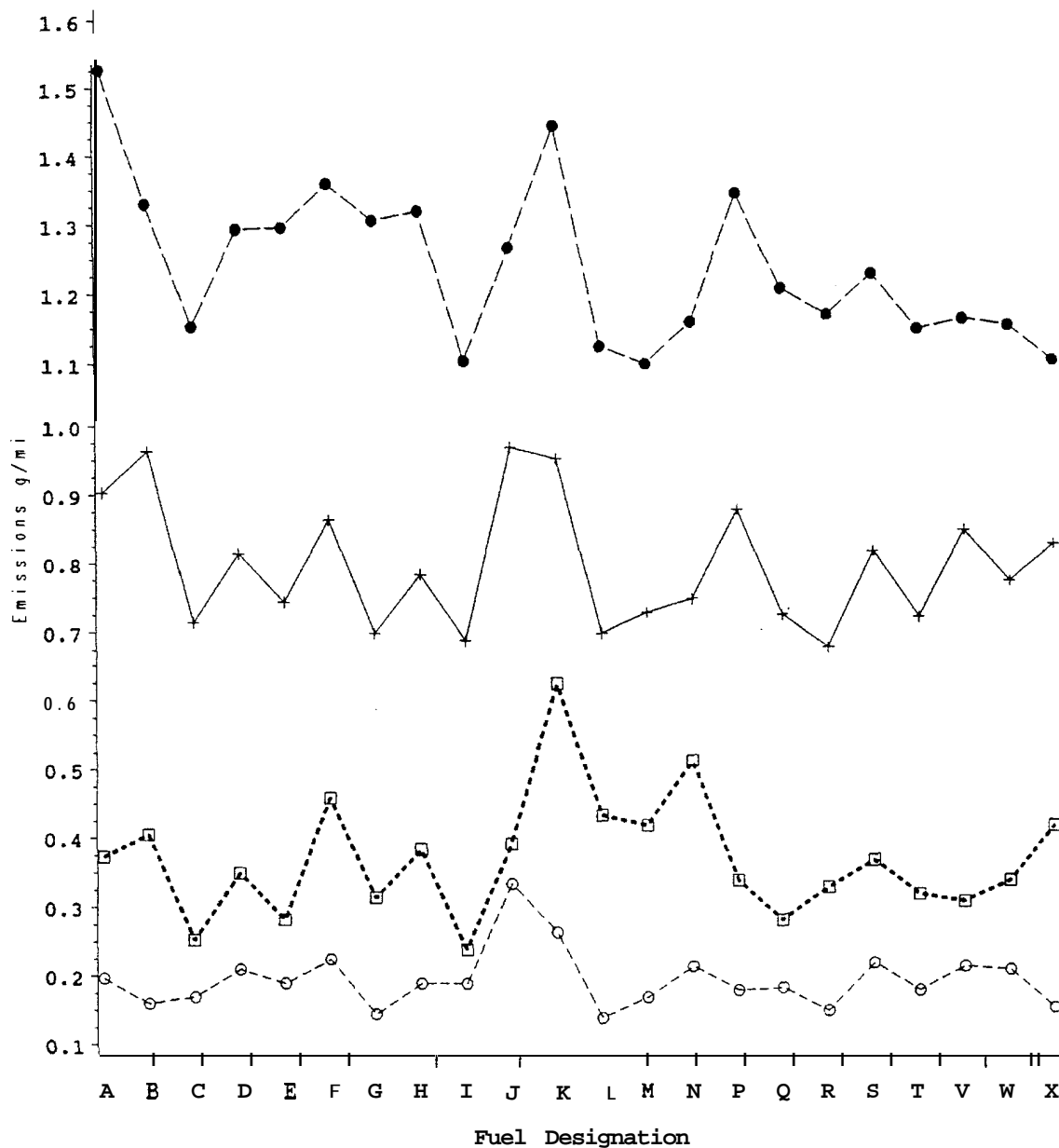
+ + + 1995 Tempo    □ □ □ 1994 Caprice  
o o o 1988        .-. .-. 1995 Suburban

Figure 5  
Emissions Test Data - NOx



+ + + 1955 Tempo    □ □ □ 1954 Caprice  
° ° ° 1959 Accord    . . . 1955 Suburban

Figure 6  
Emissions Test Data - HC



+++ 1995 Tempo    □□□ 1994 Caprice  
 ○○○ 1988 Accord    ... 1985 Suburban

*Figure 7*  
*Individual Car Effects - CO*

Car	Fuel Variable										R <sup>2</sup>
	Arom	Olef	Para	MTBE	RON	MON	T10	T50	T90	RVP	
1989 Calais			-					++			0.974
198 Oldsmobile 98			-					+			0.974
1985 Tempo			-					++			0.972
1990 Lincoln								+			0.971
1984 Caprice	-							+			0.926
1988 Accord								+			0.944
1989 Taurus								+			0.980
1990 Shadow			-					+	+		0.966
1985 Suburban			+					++	(-)		0.962
1990 Camry			-					++			0.968

Note: () indicates minor effects

**Figure 8**  
**Individual Car Effects - NOx**

Car	Fuel Variable										R <sup>2</sup>	
	Arom	Olef	Para	MTBE	RON	MON	T10	T50	T90	RVP		
1989 Calais		+	(-)				(+)				++ ++ ++	0.973
1988 Oldsmobile 98		+					(+)				++ ++ ++	0.965
1985 Tempo		+					(+)				++ ++ +	0.992
1990 Lincoln		+					+				++ ++ ++ ++ +	0.995
1984 Caprice		+					+				++ ++ +	0.994
1988 Accord		+	(-)				(+)				++ ++ ++ ++ +	0.978
1989 Taurus		+					(+)				++ ++ ++	0.991
1990 Shadow		+					(+)				++ ++ ++ +	0.995
1985 Suburban		+					+				++ ++ ++	0.990
1990 Camry		+					(+)					0.894

Note: () indicates minor effects



*Figure 9*  
*Individual Car Effects - HC*

Car	Fuel Variable										R <sup>2</sup>	
	Arom	Olef	Para	MTBE	RON	MON	T10	T50	T90	RVP		
1989 Calais		++			--			+				0.967
1988 Oldsmobile 98					-			+				0.948
1985 Tempo								+				0.993
1990 Lincoln								+				0.961
1984 Caprice								+				0.952
1988 Accord								+				0.951
1989 Taurus		+			-			+				0.973
1990 Shadow								+				0.965
1985 Suburban								+				0.988
1990 Camry		++			-			+				0.977

GASOLINE FUEL

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 08/409,074, filed in the United States Patent and Trademark Office on Mar. 22, 1995, now U.S. Pat. No. 5,593,567 which application is a continuation of U.S. patent application Ser. No. 08/077,243, filed in the U.S. Patent and Trademark Office on Jun. 14, 1993, now abandoned, which application is a division of U.S. patent application Ser. No. 07/628,488, filed in the U.S. Patent and Trademark Office on Dec. 13, 1990, now U.S. Pat. No. 5,288,393.

The present invention relates to fuels, particularly gasoline fuels, and combustion methods therefor, and methods for preparing gasoline fuels which, upon combustion, minimize the release of CO, NOx, and/or hydrocarbon emissions to the atmosphere.

One of the major environmental problems confronting the United States and other countries is atmospheric pollution (i.e., "smog") caused by the emission of gaseous pollutants in the exhaust gases from automobiles. This problem is especially acute in major metropolitan areas, such as Los Angeles, Calif., where the atmospheric conditions and the great number of automobiles account for aggravated air pollution.

It is well known that the three primary gaseous constituents, or pollutants, which contribute to air pollution due to auto exhaust are nitrogen oxides (NOx), carbon monoxide (CO), and unburned or incompletely burned hydrocarbons (i.e., hydrocarbon components originally present in the gasoline fuel which are not fully converted to carbon monoxide or dioxide and water during combustion in the automobile engine).

SUMMARY OF THE INVENTION

The present invention provides gasoline fuels from which a relatively low amount of gaseous pollutants, and in particular one or more of NOx, CO, and hydrocarbons, is produced during combustion in an automotive engine. The invention provides methods for producing gasoline fuels having such desirable properties. The invention also provides methods of combusting such fuels in automotive engines while minimizing emission of pollutants released to the atmosphere, which in turn provides a method for reducing air pollution, particularly in congested cities and the like, when large volumes of automotive fuel of the invention are combusted in a great number of automobiles in a relatively small geographical area.

The present invention also provides a petroleum refiner with knowledge of which properties of a gasoline fuel to alter, and in which direction (i.e., increased or decreased), so as to produce a gasoline fuel which will reduce or minimize NOx, CO, and hydrocarbon emissions upon combustion in an automotive engine.

The present invention, in its broadest aspect, is founded on the discovery that, when gasoline fuels are produced, for example, by blending a plurality of hydrocarbon-containing streams together so as to produce a gasoline product suitable for combustion in an automotive spark-induced internal combustion engine, improvements in emissions of one or more pollutants selected from the group consisting of CO, NOx, and hydrocarbons upon combustion of the gasoline product in such an engine system can be attained by controlling certain chemical and/or physical properties of said

gasoline product. For example, a first hydrocarbon-containing stream boiling in the gasoline range can be blended with a different hydrocarbon stream at rates adjusted so as to effect at least one of the properties of the first gasoline stream as follows:

- (1) decrease the 50% D-86 Distillation Point;
- (2) decrease the olefin content;
- (3) increase the paraffin content;
- (4) decrease the Reid Vapor pressure;
- (5) increase the Research Octane Number;
- (6) decrease the 10% D-86 Distillation Point;
- (7) decrease the 90% D-86 Distillation Point; and
- (8) increase the aromatic content

The greater the increase or decrease of the eight properties as set forth above, the greater the resulting benefit in reducing emissions of one or more of CO, NOx, and hydrocarbons.

For gasoline fuels in which one desires that hydrocarbon emissions and/or CO emissions be minimized or reduced, the principal factor influencing such emissions is the 50% D-86 distillation point, with decreases therein causing decreases in the hydrocarbon emissions. Fuels generally prepared in accordance with this embodiment of the invention have a 50% D-86 distillation point no greater than 215° F. (101.6° C.), with the hydrocarbon and CO emissions progressively decreasing as the 50% D-86 distillation point is reduced below 215° F. (101.6° C.). Preferred fuels have a 50% D-86 Distillation Point of 205° F. (96.1° C.) or less.

Best results are attained with fuels having a 50% D-86 distillation point below 195° F. (90.6° C.).

For gasoline fuels in which one desires that emissions of NOx be minimized or reduced, the principal factor influencing such emissions is Reid Vapor pressure. NOx emissions decrease as the Reid Vapor Pressure is decreased (e.g., to 8.0 psi (0.54 atm) or less, preferably to 7.5 psi (0.51 atm) or less, and even more preferably below 7.0 psi (0.48 atm)). Of secondary importance with respect to NOx emissions are the 10% D-86 Distillation Point and the olefin content. In general, decreasing olefin content (e.g., below 15 volume percent, preferably to essentially zero volume percent) and/or decreasing the 10% D-86 Distillation Point (e.g., to values below 140° F. (60° C.)) will provide some reduction in NOx emissions. However, because it is contemplated that decreases in olefin content will be more acceptable to an oil refiner than decreasing the 10% D-86 Distillation Point sufficiently to significantly affect the NOx emissions, it is believed that, as a practical matter, it will be olefin content which will be the secondary variable providing the most flexibility to an oil refiner in altering the gasoline properties to reduce NOx emissions. (This is all the more the case inasmuch as, in general, if one wishes to decrease the Reid Vapor Pressure, it is usually necessary to increase the 10% Distillation Point.) Accordingly, best results are attained when both the olefin content is below 15 volume percent (preferably to zero) and the Reid vapor pressure is no greater than 7.5 psi—with it being highly desirable, if possible, to also maintain the 10% D-86 Distillation Point below 140° F. (60° C.).

In view of the foregoing, it can be seen that many modifications of the invention are possible, depending upon which of the three pollutants one desires to reduce and the degree of reduction desired. For example, one can attain significant reductions in all three pollutants—hydrocarbons, CO, and NOx—by maintaining the 50% D-86 distillation point at or below about 215° F. (101.6° C.) and maintaining the Reid Vapor Pressure no greater than 8.0 psi (0.54 atm).

Still better reductions can be obtained by maintaining the olefin content below 10 volume percent, or maintaining the 10% D-86 distillation point below 140° F. (60° C.), with still further reductions being possible when both the olefin content and 10% D-86 Distillation Point are so maintained. Yet further reductions are possible by maintaining the 50% D-86 distillation point below 195° F. (90.6° C.), by reducing the olefin content to below 5.0 vol. % (preferably to essentially zero), by decreasing the 10% D-86 Distillation Point to below 120° F. (49° C.), and/or by maintaining the Reid Vapor pressure below 7.0 psi (0.48 atm).

The presently preferred specifications proposed for commercial use for a gasoline produced in accordance with the invention are: (1) Olefin Content of 0%; (2) Reid Vapor Pressure of 7.5 psi (0.51 atm) maximum; and (3) 50% D-86 distillation point greater than 180° F. (82° C.) but no greater than 205° F. (96° C.). However, other fuels falling within the scope of the invention are also possible, for example, fuels meeting the following criteria:

- (1) a 50% D-86 distillation point no greater than 215° F. (101.7° C.) and a Reid Vapor Pressure no greater than 8.0 psi (0.54 atm).
- (2) a 50% D-86 distillation point no greater than 205° F. (96° C.) and an olefin content less than 3 percent by volume;
- (3) a Reid Vapor Pressure no greater than 8.0 psi (0.54 atm) and containing at least 40 volume percent paraffins;
- (4) a Reid Vapor Pressure no greater than 7.5 psi (0.51 atm) and containing essentially no methyl tertiary butyl ether but less than 15 volume percent olefins.

One of the main advantages of the invention is that a less polluting gasoline fuel is provided that can be easily prepared in a petroleum refinery or the like. That is, in a typical refinery in which gasoline is produced, it is necessary or at least desirable in most instances to blend the hydrocarbon stocks so as to produce gasolines of specified Reid Vapor Pressure, olefins content, etc. Thus, the only difference is that now the refinery will blend the stocks in light of the information provided herein such that the NO<sub>x</sub>, CO, and hydrocarbon emissions are reduced as much as possible or practicable, given the individual situation (the blend stocks available, refining capacity, etc.) facing the particular refinery.

It will be understood in this disclosure and the claims to follow that the words "reduce" and "reducing" in the context of lowering NO<sub>x</sub>, CO, or hydrocarbon emissions are relative terms. Obviously, the simplest way to produce no emissions is to combust no fuel; and equally obviously, almost any combustion of a gasoline fuel will produce some emissions and thus produce greater emissions than if no fuel were combusted. However, on the assumption that the motoring public would find the consequences of combusting no fuel rather unattractive, logic dictates in the context of this invention that "reducing" is in comparison to the results achievable with other fuels. For example, for those embodiments of the invention in which the 50% D-86 Distillation Point is controlled to no more than 200° F. (93° C.), the emissions will be reduced in comparison to the otherwise identical fuel but having a higher 50% D-86 Distillation Point when combusted in the same automotive engine (or in an equivalent number of automotive engines) operating for the same time period in the same way.

#### BRIEF DESCRIPTION OF THE DRAWING

The invention can be best understood with reference to the drawing, the figures of which provide graphical or

tabular data derived from the experiments described hereinafter with respect to Examples 2 and 3.

More particularly, FIG. 1 is a graph of CO emission values for 22 different fuels tested in six different automobiles. Each data point on the graph is an average of a plurality of runs for each fuel-automobile combination.

FIG. 2 is a graph of NO<sub>x</sub> emission values for 22 different fuels tested in six different automobiles. Each data point on the graph is an average of a plurality of runs for each fuel-automobile combination.

FIG. 3 is a graph of hydrocarbon emission values for 22 different fuels tested in six different automobiles. Each data point on the graph is an average of a plurality of runs for each fuel-automobile combination.

FIG. 4 is a graph of CO emission values for 22 different fuels tested in four different automobiles. Each data point on the graph is an average of a plurality of runs for each fuel-automobile combination.

FIG. 5 is a graph of NO<sub>x</sub> emission values for 22 different fuels tested in four different automobiles. Each data point on the graph is an average of a plurality of runs for each fuel-automobile combination.

FIG. 6 is a graph of hydrocarbon emission values for 22 different fuels tested in four different automobiles. Each data point on the graph is an average of a plurality of runs for each fuel-automobile combination.

FIG. 7 is a table, based on data derived from the experiments in Examples 2 and 3, which identifies the most significant variables which increase emissions of CO when the variable is increased (as identified by one or more + signs) or which decrease emissions of CO when the variable is decreased (as identified by one or more - signs).

FIG. 8 is a table, based on data derived from the experiments in Examples 2 and 3, which identifies the most significant variables which increase emissions of NO<sub>x</sub> when the variable is increased (as identified by one or more + signs) or which decrease emissions of NO<sub>x</sub> when the variable is decreased (as identified by one or more - signs).

FIG. 9 is a table, based on data derived from the experiments in Examples 2 and 3, which identifies the most significant variables which increase emissions of hydrocarbons when the variable is increased (as identified by one or more + signs) or which decrease emissions of hydrocarbons when the variable is decreased (as identified by one or more - signs).

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to gasoline compositions having chemical and physical properties which reduce and/or minimize the amount of gaseous pollutants emitted during combustion. In particular, the invention aims to reduce and/or minimize the emissions of hydrocarbons, NO<sub>x</sub> and/or CO during combustion in an automotive engine.

Gasolines are well known fuels, generally composed of a mixture of hydrocarbons boiling at atmospheric pressure in a very narrow temperature range, e.g., 77° F. (25° C.) to 437° F. (225° C.). Gasolines are typically composed of mixtures of aromatics, olefins, and paraffins, although some gasolines may also contain such added non-hydrocarbons as alcohol (e.g., ethanol) or oxygenates (e.g., methyl tertiary butyl ether). Gasolines may also contain various additives, such as detergents, anti-icing agents, demulsifiers, corrosion inhibitors, dyes, deposit modifiers, as well as octane enhancers such as tetraethyl lead. However, the preferred fuels

contemplated in the invention are unleaded gasolines (herein defined as containing a concentration of lead no greater than 0.05 gram of lead per gallon (0.013 gram of lead per liter)). The preferred fuels will also have a Research Octane Number (RON) of at least 90. Octane value (R/2+M/2) for regular gasoline is generally at least 87 and for premium at least 92.

At present, most gasolines suitable for combustion in automotive spark-ignition engines conform to the requirements of ASTM D4814-89 specifications, which specifications are herein incorporated by reference in their entirety. Such gasolines fall into five different volatility classes, with some of the specifications therefor set forth in the following Table 1:

TABLE 1

Properties	Class A	Class B	Class C	Class D	Class E
RVP					
(psi) max	9.0	10.0	11.5	13.5	15.0
(atm) max	0.6	0.7	0.8	0.9	1.0
Dii. 10%					
(°F.) max	158	149	140	131	122
(°C.) max	70	65	60	55	50
Dist. 50%					
(°F.) min-max	170-250	170-245	170-240	170-235	170-230
(°C.) min-max	77-121	77-118	77-116	77-113	77-110
Dist. 90%					
(°F.) max	374	374	365	365	365
(°C.) max	190	190	185	185	185
End Point					
(OF.) max	437	437	437	437	437
(°C.) max	225	225	225	225	225

The most preferred gasolines produced in accordance with the invention are those which meet the requirements of one or more of the five classes specified in Table 1.

In the present invention, the gasoline is formulated, usually by appropriately blending various hydrocarbon streams in a refinery, to reduce or minimize emissions of CO, NOx, and/or hydrocarbons upon combustion in a spark-induced automotive internal combustion engine. It has been discovered in the present invention, for many automotive engines, that the amount of pollutants emitted upon combustion is closely in accord with the following equations:

## Equation 1

$$\text{CO (gm per mile)} = K_1 \times (\text{D-86 Dii. 50\% Point in } ^\circ\text{F.}) + K_2 \times (\text{D-86 Dist. 90\% Point in } ^\circ\text{F.}) - K_3 \times (\text{Vol. \% Paraffins})$$

## Equation 2

$$\text{NOx (gm per mile)} = K_4 \times (\text{Vol. \% Olefins}) - K_5 \times (\text{Vol. \% Paraffins}) + K_6 \times (\text{D-86 Dii. 10\% Point in } ^\circ\text{F.}) + K_7 \times (\text{RVP in psi})$$

## Equation 3

$$\text{HC (gm per mile)} = K_8 \times (\text{Vol. \% Olefins}) - K_9 \times (\text{Research Octane Number}) + K_{10} \times (\text{D-86 Dist. 50\% Point in } ^\circ\text{F.})$$

where each K value in the foregoing equations is a positive number. The K values will be fixed for a particular engine in a particular car but can be readily determined. For example,

for a 1988 Oldsmobile Regency 98 equipped with a 3.8 liter V-6 Engine, the K values are such that the equations are as follows:

## Equation 4

$$\text{CO (gm per mile)} = 0.00937 \times (\text{D-86 Dist. 50\% Point in } ^\circ\text{F.}) + 0.00133 \times (\text{D-86 Dist. 90\% Point in } ^\circ\text{F.}) - 0.00828 \times (\text{Vol. \% Paraffins})$$

## Equation 5

$$\text{NOx (gm per mile)} = 0.00503 \times (\text{Vol. \% Olefins}) - 0.0060 \times (\text{Vol. \% Pal-\&m}) + 0.0087 \times (\text{D-86 Dist. 10\% Point in } ^\circ\text{F.}) + 0.0159 \times (\text{RVP in psi})$$

## Equation 6

$$\text{HC (gm per mile)} = 0.00245 \times (\text{Vol. \% Olefins}) - 0.00104 \times (\text{Research Octane Number}) + 0.00109 \times (\text{D-86 Dist. 50\% Point in } ^\circ\text{F.})$$

From the foregoing equations, and from the relative sizes of the various K values and the typical values which would pertain for the properties by which the K values are multiplied (e.g., Vol. % Olefins, Research Octane Number, etc.), the following conclusions are obtained for the 1988 Oldsmobile Regency 98 and similar automobiles: For CO emissions, although decreasing the 90% D-86 distillation point has some impact on lowering CO emissions, the paraffin content and the 50% D-86 Distillation point influence such emissions much more substantially. All other things being equal, increasing the paraffin content or reducing the 50% D-86 distillation point will provide the most dramatic effects in reducing CO emissions. With best results being attained when both the paraffin content is substantially increased and the 50% D-86 distillation point is substantially reduced. In like manner, it can be seen that by decreasing the 10% D-86 Distillation Point and/or by increasing the paraffin content, some decrease in the NOx emissions will be produced. However, far more influential on the NOx emissions are the olefin content and the Reid Vapor Pressure, both of which cause substantial reductions in NOx emissions as they are substantially decreased. For hydrocarbon emissions, inspection of the equations indicates, since one is usually constrained to no more than a 5 unit change in Research Octane Number in the range of about 90 to 95, that it will not normally be practicable to alter the Research Octane Number sufficiently to have a significant impact on the hydrocarbon emissions. Accordingly, although some reduction in hydrocarbon emissions can be attained by increasing the Research Octane Number, the most practical way to significantly lower the hydrocarbon emissions while retaining other beneficial properties of the fuel is by lowering the olefin content and/or by lowering the 50% D-86 Distillation Point.

The foregoing equations also provide those skilled in the art, again as to a 1988 Oldsmobile Regency 98 and similar automobiles, with information as to how to lower the reductions of not just CO, NOx, or hydrocarbons, but also any combination thereof. For example, if one is interested in reducing the emission levels of all three, the equations show, if all other properties are held essentially constant, that reducing the Reid Vapor Pressure and the 50% D-86 distillation point will decrease the emissions of CO, NOx, and hydrocarbons. Likewise, decreases in these three pollutants can be attained by decreasing the 50% D-86 Distillation Point and decreasing the olefin content.

The above equations also lead to the following conclusions (again as to the 1988 Oldsmobile Regency and similar automobiles):

All other properties of a gasoline fuel being substantially the same,

1. As the 50% D-86 Distillation Point is progressively decreased, progressively greater reductions in CO and hydrocarbons emissions will result;
2. As the olefin content is progressively decreased, progressively greater reductions in NO<sub>x</sub> and hydrocarbons emissions will result;
3. As the paraffin content is progressively increased, progressively greater reductions in CO and NO<sub>x</sub> emissions will result;
4. As the Reid Vapor pressure is progressively decreased, progressively greater reductions in NO<sub>x</sub> emissions will result;
5. As the Research Octane Number is progressively increased, progressively greater reductions in hydrocarbon emissions will result;

- 5 A total of 22 different unleaded gasoline fuels was tested in a 1988 Oldsmobile Regency 98 automobile equipped with a 3800 cc V-6 engine. This automobile was selected because it represented a high sales volume product with close to the current state-of-the-art emission technology. The emission system was closed loop control on the air to fuel ratio with a three way catalyst system and adaptive learning capability. The automobile had been previously driven for 38,000 miles to stabilize the Octane Requirement Increase.

The properties of each of the 22 fuels are shown in the following Table 2.

TABLE 2

Blend Designation	GASOLINE PROPERTIES									
	Aromatic Vol. % by FIA	Olefins Vol. % by FL4	Paraffins Vol. % by FIA	MTBE Vol. % by IR	Research octane Number	Motor Octane Number	D86 Dist. 10% point (°F.)	D86 Dii. 50% point (°F.)	D86 sit. 90% point (°F.)	Reid Vapor Pressure psi
AR3951-1	7.60	0.2	92.20	0.0	93.6	89.2	131	209	299	9.00
AR3951-2	6.60	0.0	93.40	0.0	90.3	86.8	111	203	383	10.10
AR39513	43.30	9.5	47.20	0.0	96.1	84.5	126	235	312	8.90
AR39514	47.50	8.3	44.20	0.0	95.8	84.4	150	251	355	5.60
AR39515	38.15	0.2	61.65	0.0	91.3	82.7	166	221	284	6.37
AR3951-6	11.90	15.9	55.00	17.2	91.5	82.2	128	174	368	8.50
AR3951-7	36.80	0.6	48.30	14.3	95.0	86.1	120	224	405	9.70
AR3951-8	12.30	12.7	60.40	14.6	94.4	85.1	120	185	341	9.20
AR3951-9	44.10	11.3	44.60	0.0	96.6	84.5	128	229	305	8.80
AR3951-10	4.50	19.6	75.90	0.0	94.4	84.8	127	195	310	9.70
AR3951-11	51.60	11.6	36.80	0.0	95.9	84.0	149	308	382	6.50
AR3951-12	28.80	0.6	55.70	14.9	92.9	85.7	128	210	271	9.55
AR3951-13	14.70	17.9	51.50	15.9	91.6	82.2	127	169	392	7.90
AR3951-14	11.60	12.9	75.50	0.0	90.7	82.8	107	193	416	9.20
AR3951-15	9.50	0.0	90.50	0.0	88.6	85.1	158	207	329	6.25
ULRG	58.30	0.4	30.40	10.9	107.0	95.7	160	218	229	5.35
G3297-PJ	40.90	11.1	48.00	0.0	96.4	85.2	120	214	339	8.20
A/O 1111	19.50	4.1	76.40	0.0	90.6	84.4	123	196	282	8.80
A/O 2222	48.30	21.0	15.40	15.3	99.0	86.1	125	221	356	8.80
A/O AVE	30.70	9.5	59.80	0.0	92.2	82.7	112	218	315	8.70
ARCO EC-1	20.70	10.8	61.40	7.1	92.8	84.0	125	198	348	8.20
SU2000E	4.0	9	45.3	5.7	97.9	86.7	139	224	321	8.0

6. As the 10% D-86 Distillation Point is progressively decreased, progressively greater reductions in NO<sub>x</sub> emissions will result;
7. As the 90% D-86 Distillation Point is progressively decreased, progressively greater reductions in CO emissions will result.

And, of course, combining any of the above seven factors will lead to yet progressively greater reductions. However, as will become evident in light of the data in the examples to follow, the most important of the foregoing factors are Reid Vapor Pressure (for reducing NO<sub>x</sub>) and the 50% D-86 Distillation Point (for reducing CO and hydrocarbon emissions). Of secondary importance in reducing NO<sub>x</sub> are the olefin content and the 10% D-86 Distillation Point, with the former being of greater influence than the latter. The following Examples serve to further illustrate the inventive concept and are not intended to be construed as limitations on the invention, which is defined by the claims.

The fuels were tested in random order with no back to back runs of the same fuel. At first, only the 15 test fuels (designated AR3951-1 through AR3951-15) were run, in random order, and all more than once. However, every fifth run was conducted with fuel G3297-PJ as a control to evaluate systematic error. Each fuel was tested in accordance with the Federal Test Procedure except that (1) instead of allowing the engine between tests to cool down in still air for 10 to 12 hours at 68" to 86" F. (20.0" to 30.0" C.), the engine was subjected for 4.75 hours to a 70" F. (21.1" C.) wind of 50 miles per hour (80.5 km/hr) and (2) instead of a Clayton dynamometer, a General Electric dynamometer was used. It will be noted that the 15 test fuels were purposely blended to provide widely different values for the ten properties shown in Table 2. The emissions data derived from combusting the 15 different test fuels were then analyzed by computer program using the SAS system commercially available from SAS Institute Inc. In this program, the results of the runs with the 15 different fuels were regressed against each of the 10 variables shown in Table 2, as well as against

all possible combinations thereof, searching for an equation for each of the three pollutants of interest (NO<sub>x</sub>, CO, and hydrocarbons) defined by the minimum number of variables that gives the best surface fit based on the R squared value. As a result, the Equations 4.5. and 6 hereinbefore presented were derived as the equations which best define the amount of pollutants (in grams per mite) emitted as a function of the properties of the fuel combusted in the 1988 Regency vehicle.

After developing the foregoing equation, the other fuels shown in Table 2 were tested most in multiple runs, and

again with the G3297-PJ fuel being used in every fifth run. These fuels were tested for the purpose of checking the accuracy of the foregoing equations in forecasting emissions for new fuel, i.e., they were used as "check fuels."

The emissions data for all runs--the test, control, and check fuels--as well as the calculated emissions according to the foregoing developed equations, are tabulated in Table 3, with it being specifically noted that the order shown in Table 3 is not the exact order in which the fuels were tested

TABLE 3

Fuel Exp. Designation	CO g/mile	NO <sub>x</sub> g/mile	HC g/mile	Calculated CO g/mile	Calculated NO <sub>x</sub> g/mile	Calculated HC g/mile
1 AR3951-1	1.106	0.196	0.100	1.593	0.203	0.131
2 AR3951-2	0.948	0.186	0.094	1.638	0.201	0.127
3 AR3951-3	1.590	0.264	0.145	2.226	0.271	0.179
4 AR3951-4	2.228	0.252	0.193	2.458	0.235	0.194
5 AR3951-5	2.034	N.D.	0.157	1.938	0.218	0.146
6 AR3951-6	1.631	0.280	0.143	<b>1.664</b>	0.293	0.133
7 AR3951-7	2.335	0.232	0.166	2.238	0.233	0.147
8 AR3951-8	1.374	0.257	0.118	1.687	0.278	0.135
9 AR3951-9	<b>2.068</b>	0.286	0.165	2.182	0.281	0.177
10 AR3951-10	1.357	0.307	<b>0.134</b>	1.611	0.318	0.162
11 AR3951-11	3.752	0.273	<b>0.268</b>	3.089	0.269	<b>0.264</b>
12 AR3951-12	1.738	0.278	0.154	1.867	0.233	0.134
13 AR3951-13	2.275	0.311	0.159	1.678	0.295	0.133
14 AR3951-14	1.959	0.271	0.147	1.737	0.259	0.148
15 AR3951-15	1.654	0.190	0.114	1.628	0.183	0.133
16 ULRG	1.901	<b>0.200</b>	0.142	2.096	0.208	0.127
17 AR3951-14	1.708	0.255	0.156	1.737	0.259	0.148
18 G3297-PJ	2.267	0.273	0.187	2.059	0.262	0.160
19 G3297-PJ	1.784	0.254	0.167	2.059	0.262	0.160
20 G3297-PJ	1.975	0.288	0.160	2.059	0.262	0.160
21 G3297-PJ	2.265	0.263	0.180	2.059	0.262	0.160
22 AR3951-1	1.269	<b>0.200</b>	0.137	1.593	0.203	0.131
23 AR3951-1	1.535	<b>0.200</b>	0.135	1.593	0.203	0.131

Fuel Exp. Designation	F T P C O Emissions	FIP NO <sub>x</sub> Emissions	FIP HC Emissions	Calculated C O Emissions	Calculated NO <sub>x</sub> Emissions	Calculated H C Emissions
24 AR3951-2	1.253	0.163	0.133	1.638	0.201	0.127
25 AR3951-3	1.692	0.244	0.148	2.226	0.271	0.179
26 AR3951-4	2.835	0.274	0.235	2.458	0.235	0.194
27 AR3951-5	1.764	0.250	0.159	1.938	0.218	0.146
28 AR3951-6	1.338	0.268	0.115	1.664	0.293	0.133
29 AR3951-7	2.059	0.223	0.146	2.238	0.233	0.147
30 AR3951-8	1.633	0.271	0.140	1.687	0.278	0.135
31 AR3951-9	1.952	0.281	0.157	2.182	0.281	0.177
32 AR3951-11	3.443	0.237	0.272	3.089	<b>0.269</b>	0.264
33 AR3951-12	1.959	0.266	0.146	1.867	0.233	0.134
34 AR3951-13	2.127	0.320	0.156	1.678	0.295	0.133
35 AR3951-14	2.552	0.284	0.182	1.737	0.259	0.148
36 G3297-PJ	2.240	0.263	0.204	2.059	0.262	0.160
37 G3297-PJ	2.059	0.240	0.168	2.059	0.262	0.160
38 G3297-PJ	2.322	0.278	0.172	2.059	0.262	0.160
39 G3297-PJ	1.893	0.286	0.169	2.059	0.262	0.160
40 G3297-PJ	2.339	0.252	0.192	2.059	0.262	0.160
41 A/O 1111	1.641	0.296	0.173	1.579	0.222	0.129
42 A/O 2222	1.999	0.251	0.172	2.417	0.345	0.189
43 A/O AVE	2.162	0.298	0.210	1.798	0.248	0.145
44 A/O AVE	2.476	0.274	0.167	1.798	0.248	0.145
45 ARCOEC-1	1.651	0.271	0.139	1.810	0.257	0.146
46 ARCOEC-1	1.517	0.255	0.139	1.810	0.257	0.146
47 SU2000E	1.738	0.203	<b>0.166</b>	2.104	0.256	0.164
48 AR3951-15	1.511	0.244	0.152	1.553	0.172	0.125
49 G3297-PJ	1.862	0.284	0.161	2.059	0.262	0.160
50 AR3951-5	2.012	0.261	0.201	1.938	0.218	0.146
51 A/O 1111	1.545	0.293	0.224	1.579	0.222	0.129
52 A/O 2222	1.963	0.246	0.157	2.417	0.345	0.189
53 ULRG	1.769	0.217	0.139	2.096	<b>0.208</b>	0.127

The multiple test emissions data for each of the check fuels and the control fuel were then averaged, set against the calculated values, the deviation from the calculated value then determined, and compared against the standard deviation, which in turn was calculated from only the data pertaining to the control fuel G3297-PJ. These data are set forth in the following Table 4:

R, S, T, V, W and X were run in six different automobiles. The properties of the 22 gasolines used are shown in the following Table 5.

TABLE 5

GASOLINE PROPERTIES										
Blend Designation	Aromatics Vol. % by FIA	Olefins Vol. % by FIA	Paraffins Vol. % by FL4	M T B E Vol. % by IR	Research Octane Number	Motor Octane Number	D86 10% point (°F)	Dist. D86 50% point (°F)	Dist. D86 90% point (°F)	Reid Vapor Pressure psi
A	9.6	0.0	90.4	0.0	94.0	89.5	128	206	291	9.23
B	5.3	0.0	94.7	0.0	91.1	87.4	106	178	290	11.45
C	48.8	10.3	41.0	0.0	97.0	84.7	122	225	300	9.14
D	46.6	11.4	42.1	0.0	96.2	84.0	147	236	334	6.63
E	39.4	0.4	60.1	0.0	97.3	83.2	164	219	271	6.46
F	9.8	16.8	73.3	15.9	92.0	83.0	121	161	231	9.35
G	32.8	0.6	66.6	13.7	96.6	87.5	107	194	2%	11.54
H	12.7	15.0	72.3	14.0	94.3	84.8	119	180	302	9.88
I	46.4	12.6	41.0	0.0	97.3	849	126	220	294	8.73
J	4.8	6.2	89.1	0.0	939	849	119	188	290	9.65
K	45.6	13.6	40.8	0.0	959	83.9	135	274	370	7.60
L	31.0	0.2	68.8	14.4	93.3	85.6	125	206	262	9.43
M	15.9	15.3	68.8	15.8	92.1	82.9	114	157	368	9.77
N	12.8	11.6	75.6	0.0	90.7	83.2	107	185	403	10.51
P					89.7	85.8	144	204	318	7.07
Q	III III	II II	III III	II II	92.1	82.7	129	220	331	8.31
R	52.0	21.9	26.1	14.6	98.8	85.5	130	224	358	8.37
S	21.1	3.9	75.0	0.0	9.10	84.3	129	199	284	8.44
T	30.2	0.0	69.8	0.0	88.5	81.2	127	182	293	8.00
V	23.3	6.0	70.7	0.0	92.0	83.5	132	196	319	7.96
W	25.6	11.8	62.5	10.1	97.7	86.7	134	215	335	8.12
X	38.5	0.0	61.5	0.0	94.8	85.0	123	211	326	7.63

TABLE 4

Emis.	Fuel	Actual g/mi	Calculated g/mi	Deviation	Standard Deviation
c o	ULRG	1.835	2.096	0.261	0.205
c o	G3297-PJ	2.127	2.059	0.067	0.205
c o	Arco EC1	1.584	1.810	0.226	0.205
c o	A/O 1111	1.593	1.579	0.014	0.205
c o	NO 2222	1.981	2.417	0.436	0.205
c o	<del>A/O 2000E</del>	<del>2.378</del>	<del>2.104</del>	<del>0.386</del>	<del>0.205</del>
NOx	ULRG	0.209	0.207	0.002	0.0162
NOx	G3297-PJ	0.266	0.261	0.005	0.0162
NOx	Arco EC1	0.263	0.256	0.007	0.0162
NOx	A/O 1111	0.295	0.222	0.073	0.0162
NOx	A/O 2222	0.249	0.345	0.096	0.0162
NOx	SU2000E	0.203	0.256	0.053	0.0162
NOx	A/O AVE	0.286	0.248	0.038	0.0162
HC	ULRG	0.141	0.127	0.014	0.0142
HC	G3297-PJ	0.178	0.160	0.017	0.0142
HC	Arco EC1	0.139	0.146	0.007	0.0142
HC	A/O 1111	0.198	0.129	0.069	0.0142
HC	A/O 2222	0.165	0.189	0.024	0.0142
HC	SU2000E	0.166	0.164	0.002	0.0142
HC	A/O AVE	0.189	0.145	0.044	0.0142

It will be seen that, in most cases, the deviations shown in Table 4 are well within three times the standard deviation. In turn, this means that the equations accurately define the scientific phenomena at work within normal realms of variabilities.

## EXAMPLE 2

In this example, 22 gasoline fuels, including 15 test fuels A through N and P, one control fuel, Q, and six check fuels,

35 The automobiles (and accompanying engines) utilized were:

- 1988 Oldsmobile 98 Regency-3.8 liter V-6
- 1989 Ford Taurus-3.0 liter V-6
- 1990 Toyota Camry-2.0 liter 4 cylinders
- 1989 GM Cutlass Calais-3.8 liter V-6
- 1990 Ford Lincoln-5.0 liter V-8
- 1990 Dodge Shadow-2.5 liter 4 cylinders

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The fuels were tested in the foregoing automobiles in the same manner as described in Example 1 except that the control fuel was used in every sixth run and the Federal Test Procedure (FTP) was followed exactly. Each fuel was tested at least twice, many three times, and some four times, in each of the vehicles.

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The CO, NOx, and hydrocarbon emission data obtained by the Federal Test Procedure for each fuel in a given automobile were averaged, and then plotted respectively in the graphs in FIGS. 1, 2, and 3. (Thus, each data point in FIGS. 1 through 3 is an average of the values obtained for each automobile with the specified fuel.) Given the great number of fuels and automobiles tested, each of the three graphs shows a remarkable similarity in the overall shape of the curves in the graphs. It is clearly evident from these figures that the general effect of a given fuel is the same for different vehicles, with only the magnitude of the effect varying.

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## EXAMPLE 3

In this example, Example 2 was repeated except on the following automobiles (and accompanying engines):

- 1985 Ford Tempo-2.3 liter 4 cylinders
- 1984 GM Caprice-5.0 liter V-S

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- 3. 1988 Honda Accord-2.0 liter 4 cylinders
- 4. 1985 GM Suburban-5.7 liter V-8

The fuels were tested in the foregoing automobiles in the same manner as described in Example 2. The emission data obtained were averaged and plotted on FIGS. 4 through 6, and once again, the results show a remarkable consistency in the effects of a given fuel.

In all, for Examples 2 and 3, a total of over 500 FTP runs was made so as to provide a large enough data base to ensure the validity of the results. It should be noted that Examples 2 and 3. and the figures of the drawing **pertaining** to each, focused on automobiles and engines which were dissimilar in many respects. However, the automobiles in Example 2 all had adaptive learning computers with fuel-to-air feed-back control loops whereas those in Example 3 did not. The figures thus show that groups of cars with these similar engineering features behave similarly to changes in the fuel, which in turn shows the universality of one of the inventive concepts. The automobiles of Examples 2 and 3 were chosen because of their high commercial sales. The automobiles of Example 2 were all relatively recent models while those of Example 3 were generally older. All but one of the Example 3 automobiles had carburetor systems whereas all of those in Example 2 had fuel injection systems.

The data derived in Examples 2 and 3 were analyzed by the same computer program as described for Example 1, searching, as in Example 1, for an equation for each automobile which would provide a value for NOx, CO, and hydrocarbon emissions as a function of the minimum number of fuel properties. Not every equation so derived conformed to the generalized equation set forth hereinbefore; some, for example, showed a minor increase in hydrocarbon emissions with increases in aromatics content. Nevertheless, many of the equations did fit the generalized equation set forth hereinbefore. and more importantly, the data overall validated the fact that the most important factors as shown in the generalized Equations 1 to 3 proved almost universally most significant for each automobile.

More specifically, where much of the previous discussion was limited to 1988 Oldsmobile Regency 98 and similar automobiles. the data in tables 7 to 9—which were obtained from the data from which FIGS. 1 to 6 were derived—indicate that some variables universally or essentially universally affect emissions from automobile engines, others are limited to one or only a few vehicles. and yet others affect a particular pollutant in about 50% of the vehicles.

More specifically still, in the tables of FIGS. 7 to 9 there are indicated for each automobile tested in Examples 2 and 3 those factors which proved to be significant in increasing the specified emission when the variable is increased (as indicated by one or more + signs) and significant in decreasing the specified emission when the variable is increased (as indicated by one or more - signs). Those variables which dramatically affect emissions (i.e.. principal factors) are indicated by more than one + or - signs, with increasing numbers of + or - signs indicating increased significance for that variable. Those variables which are of least importance among the significant variables are indicated by a (+) or (-) sign. (Also shown in FIGS. 7 to 9 are the values obtained by summing the square of all the data predicted by the particular equation for each automobile for a particular pollutant and dividing by the sum of the square of all the data actually obtained for the automobile. It will be recognized that, the closer such value is to 1.0, the better the equation defines the effect under consideration. In the case of FIGS. 7 to 9, 29 of the 30 values are above 0.9 and only one is below—and that scarcely below at 0.894. Accordingly, it was determined that

the equations for each of the automobiles was statistically accurate, and that therefore the data derived therefrom—as shown in FIGS. 7 to 9—would meaningfully point to those variables which would have a statistically significant effect upon the emission characteristics from a given automobile in FIGS. 7 to 9.)

When the data of Examples 2 and 3 are analyzed as shown in FIGS. 7 to 9. the following facts stand out as most significant:

1. Decreases in the 50% D-86 Distillation Point caused decreases in CO and hydrocarbon emissions for all of the automobiles.
2. Decreases in the Olefin Content caused reductions in NOx emissions from all the vehicles.
3. Decreases in the 10% D-86 Distillation Point caused reductions in NOx emissions from all the vehicles.
4. Decreases in Reid Vapor Pressure caused reductions in NOx emissions from all the vehicles but one.

Accordingly, from the data in FIGS. 7 to 9, it can be seen that for automobiles in general that decreasing any of the variables 1 to 4 above will have a positive effect, especially for any large population of automobiles. In turn. it can be appreciated that the preferred fuels of the invention will be prepared (e.g., by appropriate blending in a refinery) so as to decrease each of the foregoing variables, and in particular. the 50% D-86 Distillation Point, the Reid Vapor Pressure, and the Olefin content, all three of which are more significantly (and easily) decreaseable in refinery practice than the 10% D-86 distillation Point.

Presently, the most commercially attractive fuel producible in accordance with the invention has the following properties: (1) Olefin Content of 0%; (2) Reid Vapor Pressure of 7.5 psi (0.51 atm) maximum; and (3) 50% D-86 distillation point greater than 180° F. (82° C.) but no greater than 205° F. (96° C.).

Where it is desired to take advantage of the emission reductions attainable by varying the 50% D-86 distillation point, this value usually is no greater than 215° F. (101.6° C.). e.g., no greater than 210° F. (98.9° C.) but preferably is greater than 205° F. (96.1° C.). e.g., less than 203° F. (95° C.), or less than 200° F. (93.3° C.). or less than 198° F. (92.2° C.), more preferably less than 195° F. (90.6° C.), e.g., less than 193° F. (89.4° C.). or less than 190° F. (87.8° C.), or less than 187° F. (86.1° C.), and most preferably less than 185° F. (85.0° C.), e.g., less than 183° F. (83.9° C.). In general, the 50% D-86 Distillation Point is above 170° F. (77° C.) and most often above 180° F. (82.2° C.).

Where it is desired to take advantage of the emission reductions attainable by varying the olefin content, this value is generally maintained less than 15 volume percent, with decreasing values providing progressively improved results. Thus. it is contemplated that each unit reduction, e.g., to values below 14, below 13, below 12, below 11, below 10, below 9, below 8, below 7, below 6, below 5, below 4, below 3, below 2, below 1 providing progressively better results, with values of 0.5 or less and essentially zero providing the best results possible.

Where it is desired to take advantage of reductions attainable by reducing the Reid Vapor Pressure, the gasoline will generally have a Reid Vapor Pressure specification of 8.0 psi (0.54 atm) max.. most often less than 8.0 psi (0.54 atm), preferably no greater than 7.5 psi (0.51 atm), even more preferably no greater than 7.0 psi (0.48 atm), and most preferably of all, no greater than 6.5 psi (0.44 atm).

Where the emissions reductions attainable by reducing the 10% D-86 Distillation Point is desired, this value is most often maintained no greater than 140° F. (71° C.), preferably



no more than 135° F. (57.2° C.), even more preferably no more than 130° F. (54° C.), and most preferably of all, no more than 122° F. (48.9° C.).

It can also be seen from the data in FIG. 7 that the paraffin content has an effect on 50% of the automobiles with respect to reducing CO, i.e., progressively increasing the paraffin content progressively decreases the CO emitted. Accordingly, where it is desired to take advantage of these facts, the paraffin content would be increased to above 40 volume percent, usually above 50 volume percent, most often to above 65 volume percent, preferably above 68 volume percent, more preferably above 70 volume percent, e.g., above 72 volume percent, even more preferably above 75 volume percent, e.g., above 77 volume percent, and most preferably, above 80 volume percent, e.g., above 82 volume percent, and most preferably of all, above 85 volume percent, e.g., above 87 or 90 volume percent.

Likewise, 60% of the automobiles shown in FIG. 9 evidenced reductions in hydrocarbon emissions when the aromatics content was increased. Where it is desired to take advantage of this fact, the aromatics content would be increased to at least 35 volume percent, preferably at least 40 volume percent.

In view of the information presented above, a petroleum refiner may take advantage of the invention by blending hydrocarbon streams boiling in the gasoline range of 77° F. (25° C.) to about 437° F. (225° C.) so as to affect at least one (and preferably more than one) of the properties of one of the streams as follows:

- (1) decrease the 50% D-86 Distillation Point;
- (2) decrease the olefin content;
- (3) increase the paraffin content;
- (4) decrease the Reid Vapor pressure;
- (5) increase the Research Octane Number;
- (6) decrease the 10% D-86 Distillation Point;
- (7) decrease the 90% D-86 Distillation Point; and
- (8) increase the aromatics content.

In such case, the petroleum refiner is, in essence, using the information provided by the present invention so as to convert a given gasoline stream into another with better properties with respect to CO, NO<sub>x</sub>, and/or hydrocarbon emissions.

It will also follow that one can increase or decrease any combination of the eight properties listed above, i.e., at least two, at least three, at least four, etc., of the properties can be increased or decreased in the direction indicated above, as well as all eight. In addition, the greater any individual property is changed in the direction indicated, the better the result, with at least 10% changes being normally used, and preferably at least 20%. In addition, one can change the property by difference instead of by percentage, for example, affecting the properties as follows:

- (a) decreasing the 50% D-86 distillation point by at least 20° F. (11.1° C.) or by at least 40° F. (22.1° C.);
- (b) decreasing the Reid Vapor Pressure by at least 1 psi (0.07 atm.) or by at least 2 psi (0.14 atm.);
- (c) decreasing the olefin content by at least 3 volume percent or by at least 5 volume percent;
- (d) increasing the paraffin content by at least 10 volume percent by at least 20 volume percent.
- (e) decreasing the 10% D-86 distillation point by at least 10° F. (5.5° C.) or by at least 20° F. (11.1° C.); and
- (f) increasing the aromatics content by at least 10 volume percent. Moreover, as would stand to reason, one could also elect to employ any combination of (a) to (f) above to produce the desired lower emission gasoline product

While the invention may be used to advantage even on a small volume basis, e.g., a single automobile operating with a fuel composition of the invention for a week or for at least 200 consecutive miles, it is clear that the benefits offered by the invention are best taken advantage of when a large number of automobiles operating with spark induced internal combustion engines requiring a gasoline fuel are powered with the fuel of the invention. In fact, the benefits of the invention increase directly with the number of automobiles which employ the fuel. Therefore, in one embodiment of the invention, on a given day, and preferably on a daily basis over a period of at least one month, at least 1,000 and more preferably at least 10,000 automobiles are provided with a fuel composition of the invention and even more preferably it is desired that the 1000+or 10,000+automobiles be provided with such fuel in a highly congested area, e.g., within the limits of a city or county encompassing a population of 500,000 or more people. Most advantageously, the amount of fuel dispensed into automobile fuel tanks within the city or county should be sufficient to effect a noticeable decrease in the amount of one or more of NO<sub>x</sub>, CO, and hydrocarbons in the air. At the present time, it is believed that, if as little as 10% of the gasoline fuel supplied to automobiles within a given city or county were a composition of the invention, a decrease in the pollution caused by one or more of these components would be obtained (assuming no significant increase in the automobile traffic within said city or county). Higher percentages, e.g., at least 25%, will yield still better results. If at least 50% of the fuel sold within a given city or county on a daily basis were a composition of the invention, it is believed, based on the data in the Examples hereinabove, that reductions in auto emissions of CO, NO<sub>x</sub>, and/or hydrocarbons at least as high as 20% as compared to the typical gasoline fuel could be observed (depending, of course, on how each of the variables is adjusted in the appropriate direction and the magnitude of such changes). Yet better results can be expected if at least 75%, even more preferably at least 90%, of the gasoline fuel were supplied on a given day from gasoline service stations within a given geographical area, e.g., a governmental district such as a city or county. Alternatively, if the same percentages pertained to a specific unit area, e.g., any 5,000 square mile (12,948 square kilometer) or 10,000 square mile (25,895 square kilometer) or any 50,000 square mile (129,476 square kilometer) area, one would expect to see reductions in one or more of CO, NO<sub>x</sub>, and hydrocarbons.

In any event, because the benefits of the invention are best realized when the gasoline fuel of the invention is supplied and combusted on a large quantity basis (i.e., large volume consumption), it is contemplated that there are many ways by which this can be accomplished, among which the following are merely illustrative:

1. Operating a fleet of automotive vehicles, numbering at least 10, preferably at least 25, with a fuel composition of the invention.
2. Operating a single automobile for an extended period of time, e.g., at least six months, or for at least 2,000 consecutive miles (3,218 kilometers), with a fuel composition of the invention.
3. Consuming at least 500 gallons (1,893 liters) of a fuel composition of the invention in one vehicle.
4. Consuming at least 2,000 gallons (7,570 liters) of a fuel composition of the invention in either one automobile or a fleet of automobiles.

Yet greater consumption can be attained by, for example: 1. Supplying, via gasoline service stations and the like, at least 1,000 vehicles, preferably at least 10,000 vehicles, per day with a fuel composition of the invention.

2. Supplying, via gasoline service stations and the like, at least 10,000,000 gallons (37,850,000 liters) per week of a fuel composition of the invention to automotive vehicles.

In order to supply and consume a gasoline composition of the invention on a large volume basis, it follows that the gasoline composition must be produced at a petroleum refinery or the like in large volumes. Typically, a refinery has a capacity to process at least 20,000 barrels per day (132,500 liters per hour), preferably at least 30,000 barrels per day (198,750 liters per hour), of crude oil and to produce at least 30,000 gallons (113,550 liters), preferably at least 50,000 gallons (189,250 liters), and most preferably at least 100,000 gallons (378,500 liters) of gasoline per day. While the invention would best be taken advantage of if all the gasoline fuel produced in a refinery were a composition of the invention, good results can be obtained if a significant fraction thereof—e.g., at least 10%—were a fuel composition of the invention. In commercial practice, it is contemplated that usual procedures will result in at least 25%, often at least 50%, and sometimes at least 75% of the daily refinery output being a fuel composition of the invention. Such output would then be delivered to gasoline service stations for introduction into automobiles, with, again, the greatest significant advantage being if all the gasoline service stations so supplied—or some significant portion thereof, e.g., at least 25%—more preferably at least 50%, and most preferably at least 75%—are located in a congested area of high population density, e.g., a city or county as described above.

Accordingly, in view of the foregoing, it will be seen that there are many ways of employing the inventive concept on a large volume basis. Obviously, the best results will be obtained when the fuel composition of the invention is so blended in a refinery or the like as to reduce the emissions of hydrocarbons, CO, and NO<sub>x</sub> to the lowest possible levels, then combusting such fuel in automobiles on a large volume basis over extended periods of time, e.g., at least one month, preferably at least six months, and with the most advantage to be realized in the most densely populated areas, e.g., counties or cities of populations exceeding 1,000,000, or more than 2,500,000, or more than 5,000,000, or in areas like Los Angeles county, more than 10,000,000 persons. To provide for the needs of such high population density areas, it may be necessary to supply the fuel composition of the invention from more than one refinery, and to deliver it to a large fraction of the gasoline service stations in such area, e.g., at least 25%, preferably at least 50%, most preferably at least 75%, so that a large number of automobiles can be supplied with the inventive fuel on a daily basis, e.g., at least 100,000, preferably at least 500,000 automobiles.

In view of the foregoing, it can be seen that the invention offers many advantages, not the least of which are the obvious health benefits associated with reduced air pollutants emitted to the atmosphere from automobiles, trucks, and other gasoline powered motor vehicles. Additionally, the invention can be put into immediate practice; current refining equipment can be employed to produce the low polluting fuels of the invention. Moreover, the invention offers the petroleum refiner a great deal of flexibility, for the invention is highly adaptable to a wide variety of hydrocarbon refinery streams. More specifically, since the description hereinbefore shows the effect of different variables, the refiner is not constrained to producing one particular fuel, but has several options, depending on what hydrocarbon streams are at hand and what properties of the fuel can be most easily altered.

By offering such flexibility with no needed hardware changes in a refinery, the invention is relatively easy to

implement—and all the more so in light of the fact that the invention can be taken advantage of without need for additives specific for reducing polluting emissions. As an example, many current fuels contain methyl tertiary butyl ether as an additive for reducing CO emissions. The present invention, however, requires no methyl tertiary butyl ether to be present. Thus, while the invention in its broadest embodiment encompasses fuels with additives that may aid in reducing such emissions, the advantages of the invention can be obtained without the necessity, for example, of a refinery having to deliberately change its practices to provide for the continuous blending of an emission-reducing additive into the fuel.

The invention, of course, as described hereinbefore, offers significant reductions in NO<sub>x</sub>, CO, and hydrocarbon emissions. Present indications are that, on a side-by-side basis, preferred fuels of the present invention offer at least a 10%, usually at least a 20%, sometimes at least 40%, reduction in emissions when tested in identical vehicles (e.g., the 1988 Oldsmobile Regency 98 described above) with identical engines and identical catalytic converter systems as compared to results obtained with a typical fuel, for example, the fuel identified in Table 2 as A/O AVE and that in Table 5 as Fuel Q. (These fuels are, in essence, identical, having been made in identical fashion but at different times; the slight differences in results shown in the two tables being within normal tolerance variations.)

It should also be recognized that the invention offers an advantage for automobile manufacturers. As government regulations progressively become more stringent in the amount of pollutants that can be emitted from motor vehicles, the present invention, by providing for a fuel inherently having properties which reduce or minimize such emissions, allows an automobile manufacturer to meet such regulations with fewer—if any—hardware design changes being needed.

It will be understood that reference hereinabove to the “D-86 Distillation Point” refers to the distillation point obtained by the procedure identified as ASTM D 8682, which can be found in the 1990 Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants, and Fossil Fuels, herein incorporated by reference in its entirety.

The FTP (Federal Test Procedure) specified hereinabove refers to Code of Federal Regulations, volume 40, “Protection of the Environment,” Subpart B, “Emission Regulations for 1977 and Later Model Year New Light-Duty Vehicles and New Light-Duty Trucks; Test Procedures, herein incorporated by reference in its entirety.

“Reid Vapor Pressure” is a pressure determined by a conventional analytical method for determining the vapor pressure of petroleum products. In essence, a liquid petroleum sample is introduced into a chamber, then immersed in a bath at 100° F. (37.8° C.) until a constant pressure is observed. Thus, the Reid Vapor Pressure is the difference, or the partial pressure, produced by the sample at 100° F. (37.8° C.). The complete test procedure is reported as ASTM test method D 323-89 in the 1990 Annual Book of ASTM Standards, Section 5, Petroleum Products, Lubricants, and Fossil Fuels, herein incorporated by reference in its entirety.

While the invention has been described in conjunction with preferred embodiments thereof, various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention. The invention has also been described with reference to examples, which are presented for illustration only, and thus no limitation should be imposed other than those indicated by the following claims:

**We claim:**

1. A method for operating an automotive vehicle having a spark-induced, internal combustion engine and a catalytic converter to yield a reduced amount of **NO<sub>x</sub>**, CO, or unburned hydrocarbons as compared to combusting fuel A/O **AVE** in said engine. the method comprising:

- (1) introducing into the engine an unleaded gasoline, suitable for combustion in an automotive engine, having a Reid Vapor Pressure less than 7.5 psi, an octane value of at least 87, a 10% D-86 distillation point no greater than 158° F., a 50% D-86 distillation point no greater than 210° F. and an olefin content less than 10 volume percent; and thereafter
- (2) combusting the unleaded gasoline in said engine;
- (3) introducing at least some of the resultant engine exhaust emissions into the catalytic converter; and
- (4) discharging emissions from the catalytic converter to the atmosphere.

2. A method for aiding in minimizing air pollution caused at least in part by exhaust emissions from gasoline-powered automobiles equipped with catalytic converters and operating within a geographical area defined by a city and its contiguous area populated by at least 500,000 persons, the geographical area also encompassing a plurality of automotive gasoline service stations,

the operation of said automobiles contributing to air pollution in said geographical area,

the method, performed by a gasoline supplier delivering at least 100,000 gallons per day of unleaded gasoline as defined below for automotive combustion in the geographical area during a one week time period, comprising:

delivering to at least 25% of the automotive gasoline service stations supplied by said supplier in said geographical area during said one week time period unleaded gasoline yielding, upon combustion, a reduced amount of **NO<sub>x</sub>**, CO, and unburned hydrocarbons as compared to Fuel A/O **AVE**, said unleaded gasoline being suitable for combustion in an automotive engine and having a Reid Vapor Pressure less than 7.5 psi, an octane value of at least 87, a 10% D-86 distillation point no greater than 158° F., a 50% D-86 distillation point no greater than 210° F., and an olefin content less than 10 volume percent.

3. A method for aiding in minimizing air pollution caused at least in part by exhaust emissions from gasoline-powered automobiles equipped with catalytic converters and operating within a contiguous geographical area having significant air pollution, the geographical area also encompassing a plurality of automotive gasoline service stations,

the operation of said automobiles contributing to air pollution in said geographical area,

the method, performed by a gasoline supplier delivering at least 100,000 gallons per day of unleaded gasoline as defined below for automotive combustion in the geographical area during a one week time period, comprising:

delivering to at least 25% of the automotive gasoline service stations supplied by said supplier in said geographical area during said one week time period unleaded gasoline yielding, upon combustion, a reduced amount of **NO<sub>x</sub>**, CO, and unburned hydrocarbons as compared to Fuel A/O **AVE**. said unleaded gasoline being suitable for combustion in an automotive engine and having a Reid Vapor Pressure less than

7.5 psi, an octane value of at least 87, a 10% D-86 distillation point no greater than 158° F., a 50% D-86 distillation point no greater than 210° F., and an olefin content less than 10 volume percent.

4. A method comprising

- (1) supplying unleaded gasoline to a fuel tank of an automobile equipped with an engine and a catalytic converter, said unleaded gasoline yielding, upon combustion, reduced emissions of **NO<sub>x</sub>**, CO, or unburned hydrocarbons in comparison to fuel A/O **AVE**, said unleaded gasoline further being suitable for combustion in an automotive engine and having a Reid Vapor Pressure less than 7.5 psi, an octane value of at least 87, a 10% D-86 distillation point no greater than 158° F., a 50% D-86 distillation point no greater than 210° F., and an olefin content less than 10 volume percent;

(2) combusting in said engine fuel drawn from said fuel tank; and

- (3) passing exhaust gases from said engine through said catalytic converter and thence to the atmosphere.

5. A method as defined in claim 4 wherein said unleaded gasoline has a 90% D-86 distillation point no greater than 315° F.

6. A method as defined in claim 5 wherein said unleaded gasoline has an olefin content less than 8 volume percent.

7. A method as defined in claim 6 wherein said unleaded gasoline has a 50% D-86 distillation point less than 195° F.

8. A method as defined in claim 6 wherein said unleaded gasoline has a 50% D-86 distillation point less than 198° F.

9. A method as defined in claim 6 wherein said unleaded gasoline has a 30% D-86 distillation point less than 200° F.

10. A method as defined in claim 6 wherein said unleaded gasoline has a 50% D-86 distillation point less than 203° F.

11. A method as defined in claim 10 wherein said unleaded gasoline has a 90% D-86 distillation point less than 300° F.

12. A method as defined in claim 6 wherein said unleaded gasoline has a 50% D-86 distillation point no greater than 205° F.

13. A method as defined in claim 6 wherein said unleaded gasoline has a 50% D-86 distillation point less than 208° F.

14. A method as defined in claim 10 wherein said unleaded gasoline has a 90% D-86 distillation point less than 300° F.

15. A method as defined in claim 4 wherein said unleaded gasoline has an olefin content less than 6 volume percent.

16. A method as defined in claim 15 wherein said unleaded gasoline has a 90% D-86 distillation point no greater than 315° F.

17. A method as defined in claim 15 wherein said unleaded gasoline has a 50% D-86 distillation point less than 195° F.

18. A method as defined in claim 17 wherein said unleaded gasoline has a 90% D-86 distillation point less than 300° F.

19. A method as defined in claim 15 wherein said unleaded gasoline has a 50% D-86 distillation point less than 198° F.

20. A method as defined in claim 19 wherein said unleaded gasoline has a 90% D-86 distillation point no greater than 315° F.

21. A method as defined in claim 15 wherein said unleaded gasoline has a 50% D-86 distillation point less than 200° F.

22. A method as defined in claim 21 wherein said unleaded gasoline has a 90% D-86 distillation point less than 300° F.

23. A method as defined in claim 15 wherein said unleaded gasoline has a 50% D-86 distillation point less than 203° F.

24. A method as defined in claim 23 wherein said unleaded gasoline has a 90% D-86 distillation point no greater than 315° F.

25. A method as defined in claim 23 wherein said unleaded gasoline has a 90% D-86 distillation point less than 300° F.

26. A method as defined in claim 15 wherein said unleaded gasoline has a 50% D-86 distillation point no greater than 205° F.

27. A method as defined in claim 26 wherein said unleaded gasoline has a 90% D-86 distillation point no greater than 315° F.

28. A method as defined in claim 15 wherein said unleaded gasoline has a 50% D-86 distillation point less than 208° F.

29. A method as defined in claim 28 wherein said unleaded gasoline has a 90% D-86 distillation point no greater than 315° F.

30. A method as defined in claim 1, 3, 4, 5, or 29 wherein said unleaded gasoline has a 50% D-86 distillation point less than 200° F.

31. A method as defined in claim 1, 3, 4, 5 or 29 wherein said unleaded gasoline has a 50% D-86 distillation point less than 195° F.

32. A method as defined in claim 1, 4, 5, 7, 9, 11, 12, 15, or 29 wherein the octane value of the unleaded gasoline is at least 92.

33. A method as defined in claim 32 wherein the Reid Vapor Pressure of the unleaded gasoline is less than 7.0 psi.

34. A method as defined in claim 3, 4, 6, 14, 17, 20, 21, 25, 26, or 29 wherein the paraffin content of the unleaded gasoline is greater than 70 volume percent.

35. A method as defined in claim 34 wherein the Reid Vapor Pressure of the unleaded gasoline is less than 7.0 psi.

36. A method as defined in claim 35 wherein the octane value of the unleaded gasoline is at least 92.

37. A method as defined in claim 36 wherein the 10% D-86 distillation point of the unleaded gasoline is no more than 135° F.

38. A method as defined in claim 28 wherein said unleaded gasoline has a 90% D-86 distillation point less than 300° F.

39. A method as defined in claim 1, 2, 3, 4, 5, or 29 wherein said unleaded gasoline has a 50% D-86 distillation point no greater than 205° F.

40. A method as defined in claim 1, 4, 6, 10, 13, 18, 22, 27, or 38 wherein the 10% D-86 distillation point of the unleaded gasoline is less than 140° F.

41. A method as defined in claim 40 wherein the octane value of the unleaded gasoline is at least 92.

42. A method as defined in claim 1, 2, 3, 4, 5, 10, 16, 18, 20, 21, 27, or 38 wherein the Reid Vapor Pressure of the unleaded gasoline is less than 7.0 psi.

43. A method as defined in claim 42 wherein the 10% D-86 distillation point of the unleaded gasoline is no more than 135° F.

44. A method as defined in claim 43 wherein the octane value of the unleaded gasoline is at least 92.

45. A method as defined in claim 2, 3, 4, 7, 11, 15, 21, 27, or 38 wherein the paraffin content of the unleaded gasoline is greater than 65 volume percent.

46. A method as defined in claim 45 wherein the octane value of the unleaded gasoline is at least 92.

47. A method as defined in claim 45 wherein the Reid Vapor Pressure of the unleaded gasoline is less than 7.0 psi.

48. A method as defined in claim 47 wherein the 10% D-86 distillation point of the unleaded gasoline is less than 140° F.

49. A method as defined in claim 48 wherein the octane value of the unleaded gasoline is at least 92.

50. A method as defined in claim 3, 4, 5, 13, 15, 18, 22, 26, or 38 wherein the paraffin content of the unleaded gasoline is greater than 72 volume percent.

51. A method as defined in claim 50 wherein the octane value of the unleaded gasoline is at least 92.

52. A method as defined in claim 50 wherein the 10% D-86 distillation point of the unleaded gasoline is less than 140° F.

53. A method as defined in claim 50 wherein the Reid Vapor Pressure of the unleaded gasoline is less than 7.0 psi.

54. A method as defined in claim 53 wherein the 10% D-86 distillation point of the unleaded gasoline is no more than 135° F.

55. A method as defined in claim 3, 4, 12, 15, 16, 18, 24, or 38 wherein the paraffin content of the unleaded gasoline is greater than 75 volume percent.

56. A method as defined in claim 55 wherein the Reid Vapor Pressure of the unleaded gasoline is less than 7.0 psi.

57. A method as defined in claim 56 wherein the octane value of the unleaded gasoline is at least 92.

58. A method as defined in claim 57 wherein the 10% D-86 distillation point of the unleaded gasoline is no more than 135° F.

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