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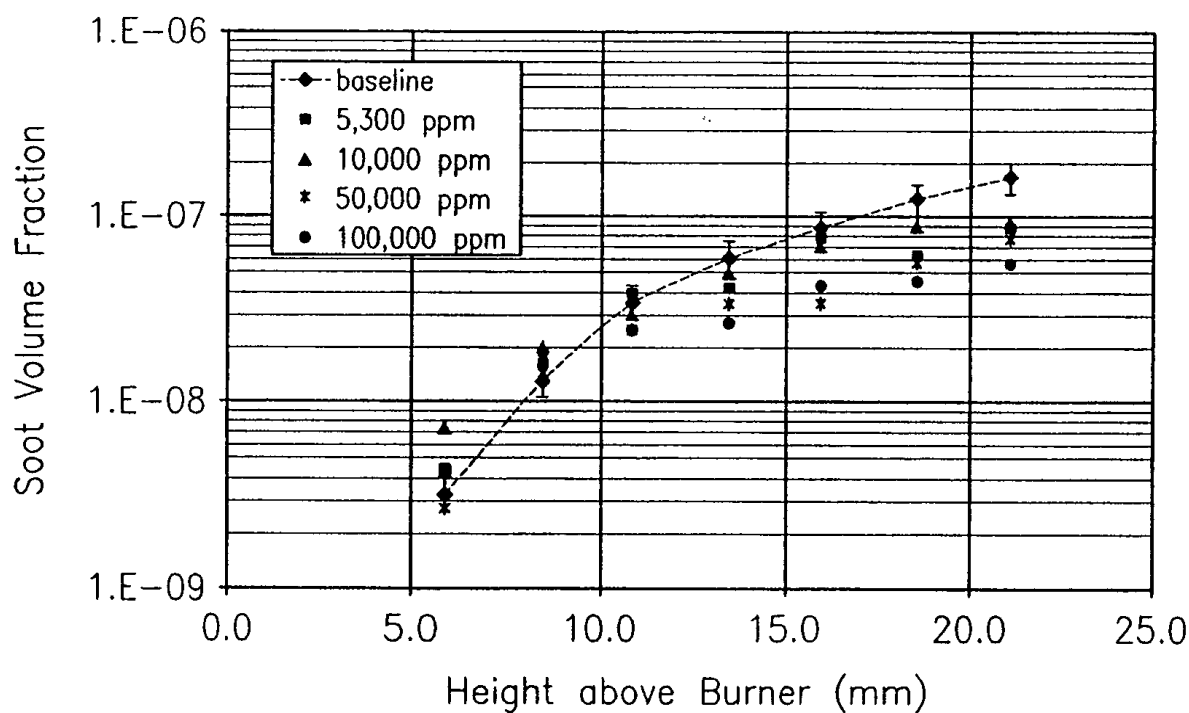
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AL HR LT LV MK(72) Inventors:
• **Colket, Meredith Bright III**
Connecticut 06070 (US)
• **Liscinsky, David Stephen**
Connecticut 06033 (US)
• **True, Bruce Scott**
Connecticut 06424 (US)(30) Priority: **29.04.2003 US 425317**(71) Applicant: **UNITED TECHNOLOGIES**
CORPORATION
Hartford, CT 06101 (US)(74) Representative: **Leckey, David H.**
Frank B. Dehn & Co.,
179 Queen Victoria Street
London EC4V 4EL (GB)(54) **Fuel-additives**

(57) A method of suppressing particulate emissions during fuel combustion comprising the steps of providing a fuel, and adding to the fuel a heterocyclic hydrocarbon structure comprising at least one nitrogen atom.

**FIG. 5**

Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a chemical composition, and method of using such a composition, for suppressing particulate emissions from combustion engines.

[0002] Particulate emissions from commercial and military turbine and diesel engines in trucks, aircraft, helicopters, ships, tanks and other power generating systems pose significant concerns. It is estimated that US military aircraft alone emit about 600,000 kg of particulate matter into the atmosphere each year. All of these combustion-generated particulate emissions are in the form of particles with diameters less than 2.5 microns (PM2.5). It is known that these small particles cause both health and environmental problems. It is therefore advantageous to adopt practices directed to the minimization of combustion-generated particulate emissions.

[0003] There are two general approaches to reducing PM2.5 emissions from gas turbine or diesel engines: (1) modification or redesign of the combustion system and, (2) modification of the fuel either by reformulation or additives. For existing engines, hardware retrofits are normally prohibitively expensive. Design of new engines and combustor systems are the result of a compromise between many competing factors and are usually not optimized to minimize particulate emissions. Considering that it took 20 years for the military to transition from JP-4 to JP-8 fuel, reformulation of the fuel is not a viable option in the near term. Therefore, the preferred approach is to use additives. This approach has been adopted readily in the diesel industry and is actively utilized for military applications to control other fuel-related concerns. The use of fuel additives is a pervasive and cost effective approach that has the potential of reducing PM2.5 emissions in all engines in the fleet.

[0004] The use of fuel-additives has been investigated with some level of success, especially for the diesel industry. However, successes have been achieved for additives at concentrations so large that they should be classified as fuel components (such as oxygen containing additives) or through the use of metals. High concentrations of oxygen-containing additives reduce the heat of combustion of the fuel and generally impose a weight penalty. Furthermore, the most effective metal compounds aggravate the environmental impact of the combustor exhaust or cause other system penalties (e.g., accelerate erosion of (coatings on) turbine blades).

[0005] What is needed is an additive that does not aggravate the pollutant character of the exhaust stream and does not create an overall system performance penalty, but is effective at a low enough concentration level that the added cost and logistics are manageable.

SUMMARY OF THE INVENTION

[0006] Accordingly, it is an object of the present invention to provide a chemical composition, and method of using such a composition, for suppressing particulate emissions from combustion engines.

[0007] In accordance with the present invention, a method to suppress particulate emissions during fuel combustion comprises the steps of providing a fuel, and adding to the fuel a heterocyclic hydrocarbon structure comprising at least one nitrogen atom.

[0008] In accordance with the present invention, a method to suppress particulate emissions during fuel combustion comprises the steps of providing a fuel, and adding to the fuel a nitrogen bearing hydrocarbon capable of decomposing so as to combine with at least one other hydrocarbon to form a nitrogen-bearing aromatic species.

[0009] In accordance with the present invention, a fuel mixture comprises a fuel, and an additive comprising a heterocyclic hydrocarbon structure comprising at least one nitrogen atom.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

FIG. 1 A diagram of the conventional path of growth from benzene to naphthalene via acetylene and/or benzene addition.

FIG. 2 A diagram of the conventional path of growth from benzene to phenanthrene via acetylene and/or benzene addition.

FIG. 3 A diagram of a reaction mechanism by which the growth of pyridine to larger aromatic species is suppressed.

FIG. 4 An illustration of the manner by which pyridine suppresses conversion of other soot forming species to larger aromatic structures.

FIG. 5 A graph illustrating results obtained by heating pyridine in a heated mixing chamber over the base of the flat flame burner.

FIG. 6 An illustration of the physical composition of pyridine, quinoline, and aniline.

FIG. 7 An illustration of several exemplary derivatives of pyridine.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0011] A central aspect of the present invention is the identification of a class of compounds which, upon addition to fuels as a fuel-additive for gas turbine or diesel engines, results in the reduction of soot emissions. Specifically, in a preferred embodiment, the addition of heterocyclic hydrocarbon structures can be added in amounts effective to reduce the mass of such soot emissions by a minimum of ten percent. A member(s) of this

class of compounds may be the sole additive or used in conjunction with other additives to maximize the soot (or particulate) reducing potential of the additive package or may be included with other additives effective at controlling/modifying other system processes, e.g., coke formation or flame stability.

[0012] The invention is based upon two key pieces of information related to the early phases of soot formation. These key pieces are: (1) the formation of aromatic and polycyclic aromatic hydrocarbons (PAH) are critical initial steps leading to particle inception and/or particle surface growth and (2) the formation of the first aromatic ring, e.g., benzene or a derivative is initiated through bimolecular reactions between two C₃H_x species and sometimes C₄H_x and C₂H_x species or reactions involving C₅H_x species, where x may be any number between 2 and 6.

[0013] PAH are critical both to the inception of soot particles and to the growth of existing particles. Hence, inhibiting the formation and growth of PAH leads to a reduction both in the number or primary particles and the total soot mass. With reference to Figure 1, there is illustrated the conventional path of growth from benzene to naphthalene via acetylene and/or benzene addition. With reference to Figure 2, there is illustrated the conventional path of growth from benzene to phenanthrene via acetylene and/or benzene addition.

[0014] An additional piece of information central to the present invention is that it is also known that nitrogen-bearing ring species (e.g., pyridine and quinoline) are low sooting compounds, despite the fact that their structures are both based on aromatic rings. Such species are analogous to benzene and naphthalene both of which are heavy sooting compounds. For example, pyridine (C₅H₅N) is known to have a low sooting tendency. Typically, it is argued that the cause of this low tendency is that with an N-atom in the ring, large pericondensed polyaromatic species cannot be formed, as the N-atom does not offer an additional unpaired electron for bonding external to the primary ring. This argument has been extended by suggesting that the lifetime of the intermediate radical (o-pyridyl) has a lifetime approximately 10,000 times shorter than the phenyl radical which is identified as an intermediate species key to soot growth. In addition, it is argued that even a 2-ringed species, e.g., quinoline (analogous to naphthalene in the pure hydrocarbon system), is not formed readily due to (relatively) higher C-H bonding strengths at the meta position.

[0015] An example of a reaction mechanism by which the growth of pyridine to larger aromatic species is suppressed is illustrated in Figure 3. First of all, the aromatic structure is much more likely to fracture as in step 2. Secondly, note that the preferred radical site (based on the fact that the C-H bond strength at this para location is 1.5 kcal/mole less than that at the meta position) formed in step 4 of the mechanism is not adjacent to the acetylenic adduct, as in the case of step 3 in the mechanism of Figure 1. Hence, this nitrogen-containing radical cannot readily add to another acetylene molecule and close the ring to form a two-ring aromatic species.

[0016] Demonstration, however, that such nitrogen bearing compounds when added in low concentrations as a fuel-additive can be utilized effectively to suppress soot formation has not been previously suggested or demonstrated.

[0017] The present invention is therefore directed to the identification of nitrogen-bearing hydrocarbons as a class of compounds to be used to suppress soot/particulate formation during combustion. An example of how pyridine suppresses conversion of other soot forming species to larger aromatic structures is illustrated with reference to Figure 4. The class of compounds that may have similar characteristics includes those that either contain nitrogen atoms imbedded into aromatic ring(s) or are precursors to the formation of such species. Hence, not only is soot formation suppressed in the presence of N-bearing aromatic rings as recognized previously, but also in a normal soot-forming (combustion) environment, the natural soot formation process can be suppressed or impeded through the addition of small amounts of species that add nitrogen to ring compounds.

[0018] A wide variety of chemical species is included in this class of compounds. Some principal examples include pyridine, quinoline, aniline and derivatives thereof.

[0019] With reference to FIG. 6, there is illustrated the physical composition of pyridine, quinoline, and aniline. With reference to FIG. 7, there is illustrated several exemplary derivatives of pyridine. For example, there is illustrated three derivatives of pyridine formed from the addition of side chains. Preferably, such side chains take the form hydrogen, alkyl groups, cycloalkyl groups, aryl groups or heterocyclic groups. In a preferred embodiment, the side chains take the form of methyl, ethyl, butyl, and amine groups. While illustrated with reference to these exemplary side chains, the present invention is not so limited. Rather, the present invention broadly encompasses fuel additives composed of heterocyclic hydrocarbon structures, preferably aromatic structures, into which is embedded one or more nitrogen atoms and any and all side chains sufficient to maintain desired fuel characteristics. For example, many such side chains are known to those in the art which could be added to heterocyclic hydrocarbon structures but which would maintain desired characteristics of the fuel mixture by acting as an antioxidant, metal deactivator, anti-icing additive, corrosion inhibitor, lubricity improver, biocide, thermos-stabilizer, or static dissipater for example.

[0020] Other compounds that decompose into cyano (CN) or amine (NH) species are included in this classification, as they may combine via processes analogous to C₃H₃ + C₃H₃ = C₆H₆ (overall) to form a nitrogen-bearing aromatic species. In fact, since one nitrogen atom has the potential of tying up 5 carbon atoms in the first

ring, and then suppressing subsequent carbon growth, the additive may also be effective through the addition of compounds that readily form CN species such as HCN within the flame. In the presence of HCN, phenyl radicals may add to HCN rather to acetylene to form benzonitrile (rather than acetylene) and thus imbedding nitrogen into the aromatic compound and inhibiting further growth to polycyclic aromatic hydrocarbons. Note that a very large fraction of the nitrogen component of these nitrogen-bearing hydrocarbons will be reduced (to molecular N_2) or oxidized prior to exiting the combustor volume.

[0021] The method of the present invention whereby nitrogen embedded heterocyclic hydrocarbon structures are added to fuel mixtures can be extended to fuel mixtures into which other additives are introduced. Such additional additives include, but are not limited to, oxygenated compounds and metal additives, specifically, nitroethane, dimethylether, and ferrocene.

[0022] The concentration level of added nitrogen to the fuel is a concern, as nitrogen oxides (i.e., NOx or the sum of NO and NO₂ emissions) are also important pollutants whose emissions are controlled. To estimate the level at which NOx emissions might be a concern when a nitrogen-bearing fuel-additive is utilized, typical emission levels can be examined. The lowest NOx emission levels for (large engine) commercial aircraft are above 30 NOxEI or 30 grams NOx (as NO₂) per kilogram of fuel. More typically, these emission levels are closer to 40-70 grams NOx (as NO₂) per kilogram of fuel, depending on the size class of the engine. Goals for future engines cruising at or near the ozone layer are closer to 10 NOxEI. Hence, a level of nitrogen in the fuel that has the potential of producing an emissions index no more than 2 appears acceptable. If a significant amount of the fuel nitrogen is fully reduced to N_2 , rather than converted to NOx emissions, then this constraint can be relaxed. Such phenomena is well-known in the literature based on studies of burning coal and synthesized liquid fuels from coal gasification/liquefaction or from shale oil.

[0023] Assume that pyridine is the selected additive compound. A limit of 2 NOxEI from the nitrogen in the fuel can be readily converted to a limit of 600 ppm of nitrogen in the fuel on a mass basis. This concentration suggests a limit of 3400 ppm of pyridine (or its equivalent) in the fuel on a mass basis. As mentioned just above, in the case that some of this 'fuel-bound' nitrogen can be converted into molecular nitrogen, these low limits can be relaxed. There is a reasonable likelihood that this 'upper limit' to the additive concentrations may be increased at least by a factor of 2-3 due to a reduction of this 'fuel-N' into molecular nitrogen in the primary zone of the combustor. Hence, a design upper limit of additive levels of pyridine is anticipated to be in the range of 6000-9000 ppm.

[0024] A "heterocyclic hydrocarbon structure" is preferably a stable 5- to 7- membered monocyclic or bicyclic or 7- to 10- membered bicyclic heterocyclic ring which

may be saturated, partially unsaturated, or aromatic, and which consists of carbon atoms and from 1 to 4 heteroatoms independently selected from N, O and S, preferably N only.

Example 1. The claim that low levels of added pyridine can reduce soot emissions from a flame has been demonstrated. The effect of pyridine as a fuel-additive during the combustion of heptane/toluene in a fuel-rich, laminar premixed flame under laboratory conditions was examined. A baseline fuel mixture of 90% heptane/10%toluene was utilized to simulate the alkane/aromatic mixture of JP-8. The fuel was prevaporized and premixed with air and with or without the additive, pyridine, in a heated mixing chamber and fed to the base of the flat flame burner. Volume fractions of soot were measured as a function of height above the burner.

[0025] Results are illustrated with reference to Figure 5. Measurements of soot volume fractions using the baseline fuel are provided, along with the typical measurement uncertainty. In addition, the soot volume fractions as a function of height are provided for flames in which various levels of pyridine have been mixed with the fuel. Even for the lower additive levels of 5300 ppm (volume fraction), a substantial reduction in the soot volume fraction is observed. While there is scatter in the data, the average fractional reduction above a flame height of 13 mm is 35%. For all these flames, the fractional reduction in the soot is noticeably greater than a simple dilution effect anticipated in blending a sooting and a non-sooting fuel.

[0026] In addition, soot particle samples were collected and analyzed. Photomicrographs (from a scanning electron microscope) of the soot samples were used to determine the primary particle size. They demonstrate that the soot particles from the pyridine-seeded flame are actually larger than for those for the non-additized flame. A typical increase in particle size is approximately 10%.

[0027] Normally, it is believed to be desirable to reduce both soot mass and soot particle size. In fact usually, these parameters are related. In this case, however, the soot mass has decreased while the particle size has increased. This result implies a non-linear reduction in the particle number density, desirable for health reasons. An estimate of the reduction in soot number density can be made for these flames studied, using the fractional changes. For a given soot mass (M), the particle number density (N) is inversely proportional to the cube of the particle diameter (d), i.e., $M = N\pi d^3/6$. Hence we find that for the flame with added pyridine described above, the 35% reduction in soot mass and the 10% increase in particle diameter results in a computed 50% reduction in soot number density. Hence, pyridine simultaneously reduces both soot mass and number density.

[0028] It is apparent that there has been described above a chemical composition, and method of using such a composition, for suppressing particulate emissions from combustion engines which fully satisfies the

objects, means, and advantages set forth previously herein. While the present invention has been described in the context of specific embodiments thereof, other alternatives, modifications, and variations will become apparent to those skilled in the art having read the foregoing description. Accordingly, it is intended to embrace those alternatives, modifications, and variations as fall within the broad scope of the appended claims.

Claims

1. A method of suppressing particulate emissions during fuel combustion, comprising the steps of:

providing a fuel; and
adding to said fuel a heterocyclic hydrocarbon structure comprising at least one nitrogen atom.

2. The method of claim 1 wherein said adding step comprises adding an aromatic structure comprising at least one nitrogen atom.

3. The method of claim 2 wherein said adding step comprises adding a heterocyclic hydrocarbon structure selected from the group consisting of pyridine, quinoline, aniline and derivatives thereof.

4. The method of any one of the preceding claims wherein said adding step comprises adding a heterocyclic hydrocarbon structure comprising at least one side chain.

5. The method of claim 4 wherein said adding step comprises adding said heterocyclic hydrocarbon structure comprising at least one side chain wherein said at least one side chain is selected from the group consisting of hydrogen, alkyl groups, cycloalkyl groups, aryl groups, and heterocyclic groups.

6. The method of claim 4 wherein said adding step comprises adding said heterocyclic hydrocarbon structure comprising at least one side chain wherein said at least one side chain is selected from the group consisting of ethyl groups, amine groups, butyl groups, and methyl groups.

7. The method of any one of claims 4 to 6 further comprising the step of selecting said at least one side chain so as to obtain at least one desired characteristic of said fuel.

8. The method of any of claims 4 to 7 wherein said adding step comprises adding said heterocyclic hydrocarbon structure functions as a substance selected from the group consisting of antioxidants,

metal deactivators, anti-icing additives, corrosion inhibitors, lubricity improvers, biocides, thermo-stabilizers, and static dissipaters.

9. The method of any of the preceding claims comprising the additional step of adding at least one additional fuel additive.

10. The method of claim 9 wherein said additional fuel additive comprises an oxygenated compound.

11. The method of claim 10 wherein said adding said oxygenated compound is selected from the group consisting of nitromethane and dimethylether.

12. The method of claim 9 wherein said additional fuel additive comprises a metal additive.

13. The method of claim 12 wherein said metal additive comprises ferrocene.

14. The method of any one of the preceding claims wherein said heterocyclic hydrocarbon structure is added to said fuel at a concentration less than 9000 ppm.

15. The method of claim 14 wherein said heterocyclic hydrocarbon structure is added to said fuel at a concentration less than 6000 ppm.

16. The method of claim 15 wherein said heterocyclic hydrocarbon structure is added to said fuel at a concentration less than 3400 ppm.

17. The method of any one of the preceding claims wherein said heterocyclic hydrocarbon structure is added in an amount sufficient to reduce a soot mass formed during said fuel combustion by at least 10%.

18. The method of any one of claims 9 to 13 wherein said fuel additive is added at a combustion of at least 50 ppm.

19. A method of suppressing particulate emissions during fuel combustion, comprising the steps of:

providing a fuel; and
adding to said fuel a nitrogen bearing hydrocarbon capable of decomposing so as to combine with at least one other hydrocarbon to form a nitrogen-bearing aromatic species.

20. A fuel mixture comprising:

a fuel; and
an additive comprising a heterocyclic hydrocarbon structure comprising at least one nitrogen atom.

21. The fuel mixture of claim 20 wherein said heterocyclic hydrocarbon structure comprises an aromatic structure comprising at least one nitrogen atom.
22. The fuel mixture of claim 20 wherein said heterocyclic hydrocarbon structure is selected from the group consisting of pyridine, quinoline, aniline, and mixtures thereof. 5
23. The fuel mixture of any one of claims 20 to 22 wherein said heterocyclic hydrocarbon structure comprises at least one side chain. 10
24. The fuel mixture of claim 23 wherein said at least one side chain is selected from the group consisting of hydrogen, alkyl groups, cycloalkyl groups, aryl groups, and heterocyclic groups. 15
25. The fuel additive of claim 23 wherein said at least one side chain is selected from the group consisting of an ethyl group, an amine group, a butyl group, and a methyl group. 20
26. The fuel mixture of any of claims 20 to 25 wherein said heterocyclic hydrocarbon structure is present at a concentration less than 9000 ppm. 25
27. The fuel mixture of claim 26 wherein said heterocyclic hydrocarbon structure is present at a concentration less than 6000 ppm. 30
28. The fuel mixture of claim 27 wherein said heterocyclic hydrocarbon structure is present at a concentration less than 3400 ppm. 35
29. The fuel mixture of any one of claims 20 to 28 wherein said additive is present in an amount effective to reduce a soot mass formed during said fuel combustion by at least 10%. 40
30. A method of suppressing particulate emissions during fuel combustion, comprising the steps of:
 - providing a fuel; and
 - adding to said fuel an aniline structure. 45
31. A fuel mixture comprising:
 - a fuel; and
 - an additive comprising an aniline structure. 50
32. Use of a heterocyclic hydrocarbon structure comprising at least one nitrogen atom, or an aniline structure for suppressing particulate emissions during fuel combustion. 55

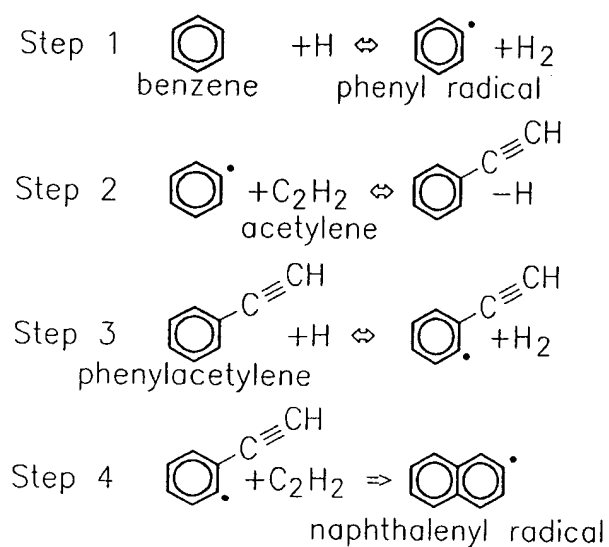


FIG. 1

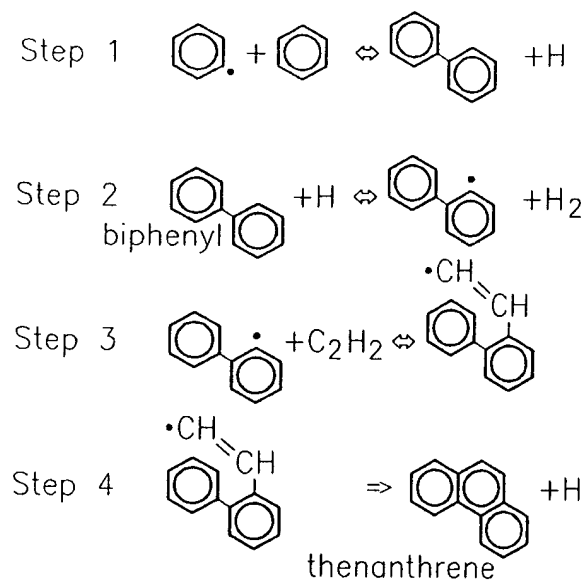


FIG. 2

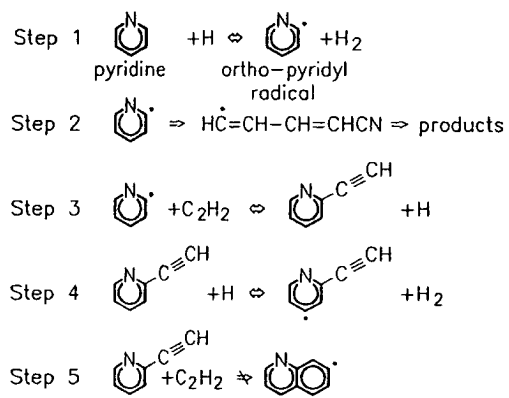


FIG. 3

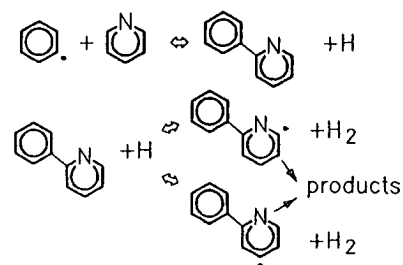


FIG. 4

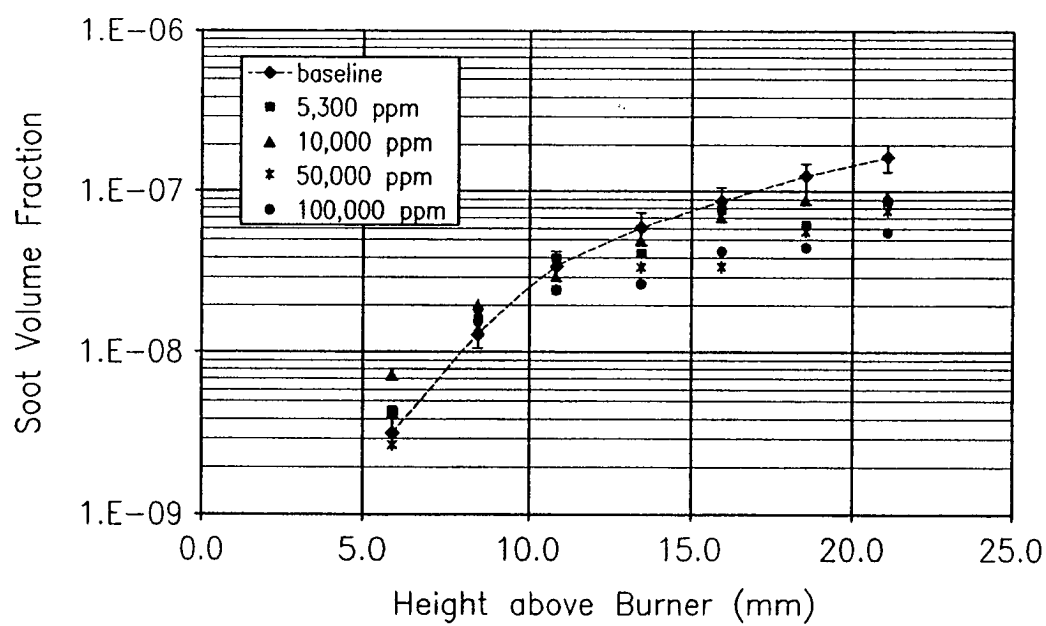


FIG. 5

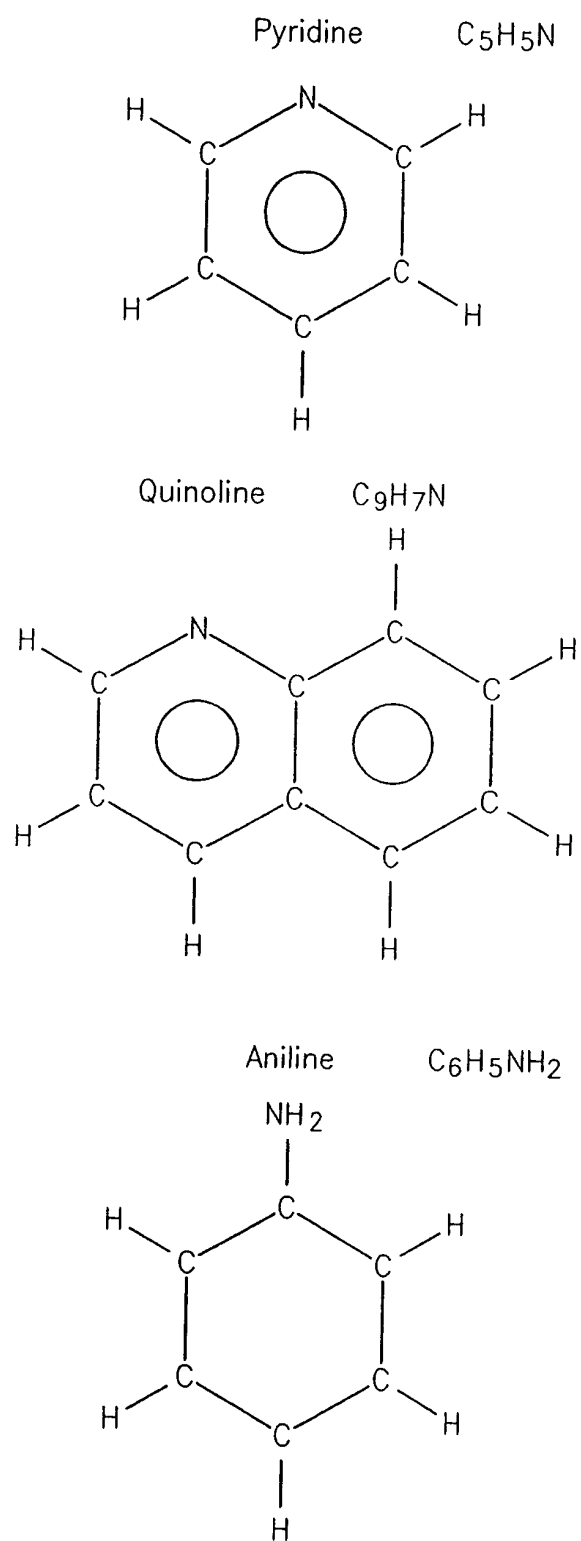


FIG. 6

Pyridine derivatives

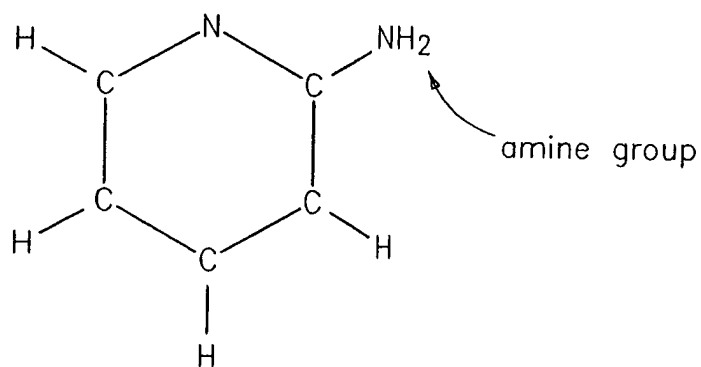
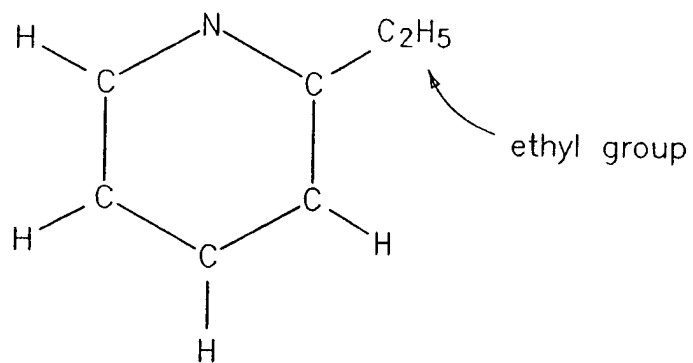
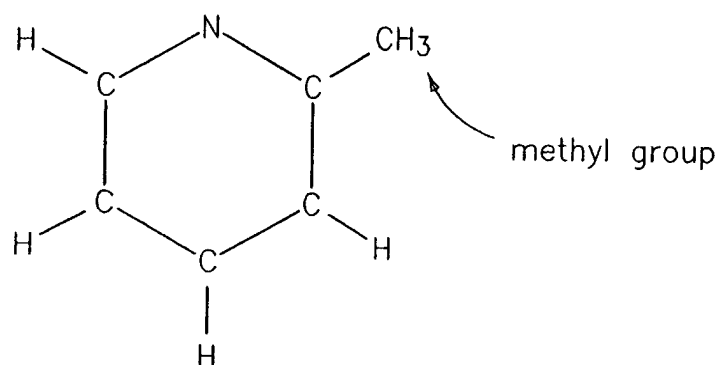


FIG. 7