

[54] COMPOSITION FOR TREATING AQUEOUS
ALKALINE FUEL

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[58] Field of Search 44/1 R, 4, 5, 50, 51

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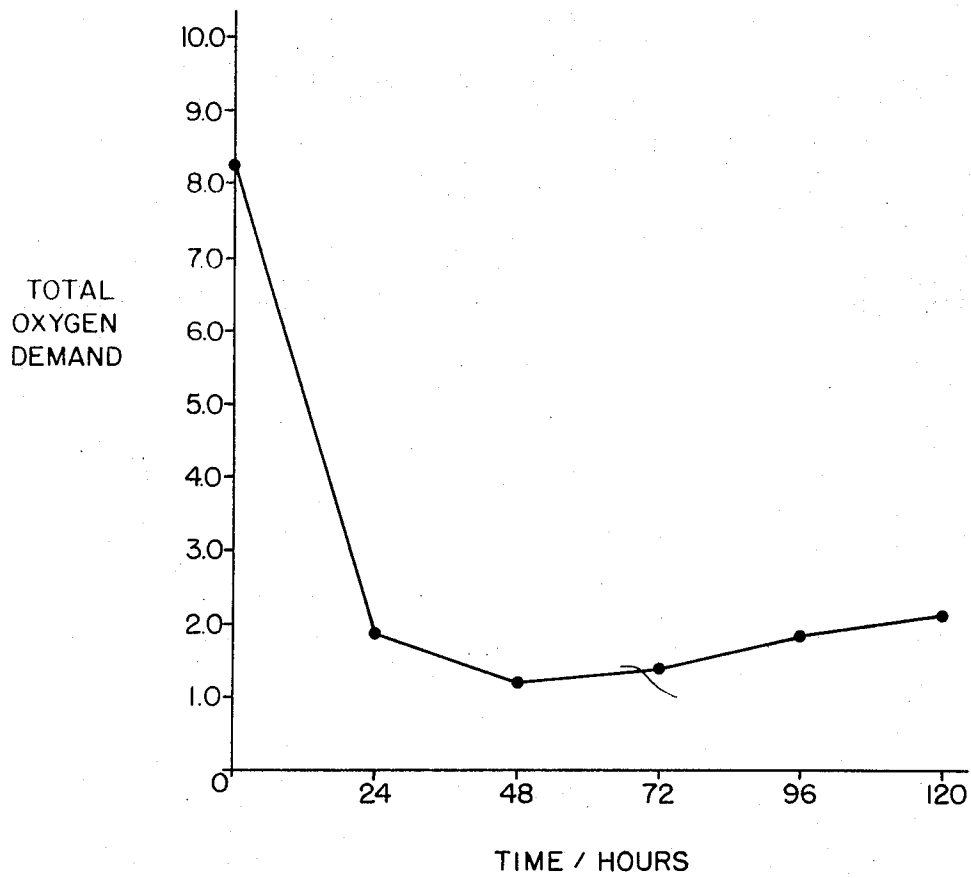
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[57] ABSTRACT

Method for improving the burning characteristics of aqueous alkaline fuels by the addition of a sequestered metal ion as catalyst to promote oxidation of water soluble organic matter and carbon. In the Kraft process the method also substantially reduces the proportion of sodium sulfide in the flue gas.

An additive consisting of a water soluble salt of manganese, copper, iron, tin, nickel or cobalt or mixtures of these metals is solubilized in an aqueous medium at an alkaline pH with a conventional sequestering agent and added to the aqueous fuel in proportions of about 2 to about 50ppm based on the metal ion. The additive is stable and soluble in the aqueous fuel. Oxygen demand of slag is substantially reduced and slag is softer and more friable.

16 Claims, 1 Drawing Figure



COMPOSITION FOR TREATING AQUEOUS ALKALINE FUEL

FIELD OF INVENTION

The present invention relates to compositions of matter and process for the combustion of aqueous alkaline fuel to improve the burning characteristics and reduce the adverse effects of combustion products on the structures with which they come in contact. More particularly the invention is concerned with the combustion of aqueous alkaline fuels in recovery boilers in paper making processes.

BACKGROUND OF INVENTION

The combustion of aqueous alkaline materials is employed in processes where the process by-products have sufficient calorific value so that the combustion of the material readily takes place and the heat generated thereby can be advantageously used in the process or where chemicals involved in the treatment process can be recovered from waste materials by combustion thereof. The most notable example of this is encountered in paper making processes such as the "Kraft" sulfate process.

The production of pulp from wood by the "Kraft" process is practiced on a world-wide scale. The process yields a high strength pulp suitable for many of the heavier applications of paper products, e.g. sturdy cartons, bags, wrappings and the like. The process consists in the digestion of wood chips, primarily conifers, in a water solution of sodium hydroxide and sodium sulfide under heat and pressure so that substantial delignification takes place along with some loss of cellulose and other sugar polymers. The resulting solution and a portion of the washings from the pulp recovery constitutes the so called weak black liquor which is then subjected to concentration by flash evaporation until the total solid content has reached 55 to 65 percent, which after concentration is referred to as black liquor.

At this point the black liquor has sufficient calorific value to support combustion and is thus directed into the recovery boilers where the useful heat derived from combustion is applied to the evaporation of the weak black liquor. Another objective of this operation is the recovery of sodium carbonate and sodium sulfide, both of which emerge at the base of the recovery boiler as a molten stream which is taken up in water, subsequently treated with calcium hydroxide to yield the so called white liquor for the digestion of fresh charges of wood chips.

The recovery boilers employed in the combustion of the black liquor are frequently beset by fouling problems due to a constant flow upwards past the super heaters and economizers of the boiler apparatus of dust laden flue gas. The gas borne particulate matter may amount to as much as 5 percent of the recovered chemicals. The bulk of the of the flue dust is trapped on the surface of high voltage electrodes and removed and redissolved in the black liquor for subsequent reprocessing. A significant fraction of the flue gas, however, deposits on the super heaters and economizer of the boiler. These deposits can develop to a thickness which impedes heat transfer as well as the free movement of the combustion gases to the stack. The process of the build-up of such deposits is referred to herein as slagging and the deposits themselves are referred to as

slag. This is not to be confused with the smelt which comprises the fused chemicals recovered at the bottom of the recovery boiler.

Recognizing that the build-up of slag within the recovery boilers is detrimental to the operation of the boiler, it is common practice to resort to soot blowing procedures, such as, discharge of super heated steam against the affected surfaces, or mechanical actions such as manual tamping of the sections where slag build-up has occurred. Regardless of these procedures however, shutdown of the whole recovery boiler plant is necessitated periodically in order to remove the accumulated slag. Thus, in spite of soot blowing, and other procedures designed to remove slag from the boiler surfaces it has been found that slag continues to deposit and build-up within the boiler.

Attempts have been made to alter the fuel itself in order to reduce slag deposition. These attempts have primarily involved the injection of finely powdered additives, principally based on magnesium oxide, into the systems by either injecting the additive into the flame zone or slurring the additive into the black liquor. These techniques however, have met with failure in that the frequency of maintenance shutdowns have not been reduced nor has there been a noticeable reduction in slag deposition or a noticeable improvement in the removal characteristic of the slag itself.

OBJECTS OF INVENTION

Accordingly, it is an object of this invention to provide an additive for aqueous alkaline fuels to make the slag formed during combustion of the fuel more readily removed from boiler surfaces in which the fuel is being burned.

It is another object of this invention to provide an additive which is solublized in the aqueous alkaline fuel so that it is effectively present during combustion of the fuel.

Another object of this invention is to provide an additive which substantially reduces the total oxygen demand of the by-products of combustion in the flue gas so that slag deposited on boiler parts is more friable and more readily removed.

These and other objects and advantages of this invention will become apparent from the detailed description of the invention and claims set forth hereinafter and from reference to the FIGURE.

BRIEF DESCRIPTION OF THE FIGURE

The FIGURE represents graphically the reduction of total oxygen demand of particulate matter borne in the flue gas of a "Kraft" process recovery boiler plotted over a period of time.

SUMMARY OF THE INVENTION

I have found that the addition of small but effective amount of sequestered catalyst metals selected from the group consisting of manganese, copper, iron, tin, nickel, cobalt or mixtures thereof, substantially reduces the total oxygen demand of the products formed during combustion of aqueous alkaline fuels thus producing a deposit having a higher fusion temperature which is more friable and readily removed from boiler surfaces. By use of sequestering agents the catalyst metal ions remain solublized in alkaline and sulfide conditions encountered in aqueous alkaline fuels, particularly black liquor produced during the "Kraft" paper making pro-

cess. By maintaining the catalyst metal ions in a solublized condition in accordance with this invention, I have found that effective amounts are present in the combustion zone so that the catalytic oxidative characteristics of the catalyst metal are effective in more completely oxidizing combustion by-products so that the deposited slag is more friable and readily removed from the boiler surfaces.

The novel additive composition of this invention is formed from a water soluble salt of a catalyst metal selected from the group consisting of manganese, copper, iron, tin, nickel, cobalt and mixtures thereof. The sequestering agent employed in the additive of this invention is not critical and any conventional sequestering agent is employed with good results. The additive is dissolved in water and maintained at an alkaline pH in order to insure activation of the sequestering agent prior to use in the invention.

In use, the solubilized additive is preferably premixed with the aqueous alkaline fuel just prior to its injection into the combustion zone. The amount of additive utilized may vary depending upon the composition of the aqueous alkaline fuel, as will be discussed hereinafter, however, good results are achieved when the additive is metered at the rate of between about 5 ppm and 50 ppm of catalyst metal ion.

DESCRIPTION OF INVENTION

Although the following description will be in connection with black liquor produced as a result of the "Kraft" paper making process, it should be clear that the invention and the principles upon which it is based will be applicable to the burning of any aqueous alkaline fuel where build-up of slag within a furnace or boiler where the fuel is being burned is a problem.

An analysis of particulate matter derived from flue gases in the burning of black liquor in the "Kraft" paper making process indicates that the principal components of the particulate matter are sodium carbonate, sodium sulfate, sodium sulfide, carbon, water soluble organic matter, insoluble matter (primarily calcium carbonate, calcium clays and iron oxide) and sodium chloride. It is believed that the slag which accumulates on the boiler surfaces is difficult to remove because of its low fusion temperature and a natural internal cohesive strength due to bonding properties of associated organic materials. Substantial reduction or elimination of sodium sulfide, elemental carbon and soluble organic matter will result in a particulate composition which has a higher fusion point and is more friable.

Elimination or substantial reduction of these three undesirable elements of the particulate composition is most readily effected by oxidation in view of the nature of the combustion process involved. However, the introduction of additional oxygen into the combustion zone is impractical and undesirable, particularly in a black liquor recovery boiler in view of the fact that oxygen has a tendency to adversely effect the sulfidity of material coming off the primary burning zone in the recovery boiler unit. Sulfidity is that portion of the sodium ions present as sodium sulfide, which is one of the chemicals recovered in the smelt.

Certain metal elements of variable valence such as copper, manganese, iron, nickel and cobalt are known to be oxidation catalysts and have been used to promote improved burning in fossil fuels. However, the use of these catalysts in aqueous alkaline fuels has been re-

stricted due to the fact that these metals are generally insoluble under conditions encountered in the fuels.

The present invention provides an additive in which catalyst metal ions selected from the group consisting of manganese, copper, iron, tin, nickel and cobalt or mixtures thereof, are provided in a form which they are stable and soluble under alkaline conditions and more particularly are soluble in the presence of conditions of alkalinity and sulfidity encountered in the black liquor of the "Kraft" process. The catalyst metal ions are provided from their water soluble salts such as acetate, sulfate, chloride, bromide, iodide and the like. The additive of this invention can employ a single species or a mixture of species of catalyst metal ions with equally good results.

To insure stability and solubility under the alkaline conditions to be encountered in an aqueous alkaline fuel, the catalyst metal ions are sequestered prior to their introduction into the aqueous alkaline fuels. Conventional sequestering (chelating) agents are used such as for example; polyamines, such as ethylene diamine, triethylene tetraamine; hydroxy polycarboxylic acids, such as, tartaric, malic, citric and the like; and N substituted carboxylic acids, such as ethylene diamine tetraacetic acid and nitrilotriacetic acid. These chelating or sequestering agents are by way of example only and it should be understood that other conventional chelating or sequestering agents may be used with equal effectiveness.

The additive of this invention when solubilized and ready for use is essentially an aqueous alkaline solution of the catalyst metal ion and a sequestering agent, although minor amounts of other ingredients, such as an antioxidant, may also be included to improve stability or shelf life of the solubilized additive. The catalyst metal ion is supplied from the water soluble salt of the catalyst metal ion such as the acetate, sulfate, iodide, bromide, chloride and the like. The solubilized additive, which has a pH preferably on the order of 9 to 10, is alkaline in order to initiate the sequestering action of the sequestering agent. The total proportions of the ingredients in the additive are not critical, except set forth below, although it is preferred to maintain the total solids content of the additive between about 25% to about 55% in order to avoid phase separation problems such as may occur if the solubilized additive is subjected to low temperatures.

Although, as mentioned above, the total proportions of the additive are not critical, the relative proportion of catalyst metal ion to sequestering agent is important in maintaining stability of the additive.

In determining the proportions of catalyst metal ion and sequestering agent it is important that at least the stoichiometric amount of sequestering agent required to sequester the metal ion be present in the additive. It is preferred, moreover, to use an excess of sequestering agent since it does not diminish the effect of the catalyst metal ion and the excess sequestering agent acts to sequester other catalyst metal ions which are normally present in the aqueous alkaline fuel thus enhancing the effectiveness of the additive of this invention.

Due to the catalytic effect of the additive of this invention, relatively minor amounts are effective in improving the friability and removability of slag formed during the combustion of aqueous alkaline fuels. The additive is effective in amounts as low as 2 parts per million based on catalyst metal although the results are

improved with increasing amounts of catalyst metal in the fuel. The presence of an excess amount of additive in the fuel is not detrimental although in the interest of economy it is preferred that the additive be present in concentrations of about 20 to 50 ppm, based on catalyst metal.

The following specific examples describe the manner in which certain embodiments of the novel additive of this invention are prepared and used and the beneficial results obtained thereby. Although the examples described specific, embodiments, the invention is not to be construed as being limited to the particular embodiments set forth in the examples.

EXAMPLE I

The following formulation were prepared and tested for solubility-stability in aqueous alkaline fuels.

Formula A

Manganese acetate	5.82%
Sodium hydroxide	10.0%
Tartaric Acid	15.8%
*Sodium Sulfite	0.2%
Water	68.2%

*Sodium sulfite is present as an antioxidant.

Formula B

Ferrous Sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	3.8%
Manganous Sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$)	2.5%
Tartaric Acid	8.3%
Triethanolamine	21.2%
Tetra sodium ethylene dinitrilo tetra acetate	8.2%
Sodium hydroxide	11.9%
Water	44.1%

The percentages in the foregoing formulations are expressed as percent by weight.

100 to 120 ppm of each of the foregoing additive formulations were then placed in a test solution prepared to duplicate the alkaline and sulfidity conditions encountered in black liquor fuel. The test solution was 1.0N with respect to NaOH and 0.1N with respect to sodium sulfide.

After 24 hours there was no evidence of precipitation from the test solution despite the fact that the solubility products of metal sulfides and hydroxides been exceeded in the test solutions.

EXAMPLE II

Formula B of Example I was field tested in an 800 ton recovery unit operating in a paper mill using the "kraft" sulfate process. Particulate flue gas samples were taken during the operation of the recovery unit from a duct between the economizers section and cyclone of the recovery unit. Formula B additive was continuously added to the black liquor in the salt cake mixing tank of the recovery unit at the rate of 100-120 ppm of additive (about 2 ppm based on catalyst metal ion) per million parts of black liquor. A sample was taken prior to treatment in accordance with this invention, and at twenty four hour periods thereafter for 4 days. Each sample of particulate matter was tested for carbon content, soluble organic content and sodium sulfide content.

The following test procedures were utilized:

CARBON CONTENT

A 30 gram portion of particulate sample was placed in a 700 ml beaker and agitated while 300 to 350 ml of distilled water was introduced into the beaker. The slurry thus formed was filtered through No. 2 filter paper without employment of suction and the residue on the filter paper was washed with distilled water until the washing had a pH of 7 to 8. The paper was dried to constant weight, weighed and then ignited to constant weight and the weight of the ash determined. Percent carbon was reported as:

Percent carbon=(insolubles minus ash) : 100/30.00

15 Determination of water soluble organic matter by COD (Chemical oxygen demand)

The filtrate collected in the carbon determination is made up to 500 ml with distilled water. 50 ml. of the solution is placed in a flask, acidified with 50 ml of 1.0 N H_2SO_4 and boiled gently for 10 to 15 minutes to expel H_2S and CO_2 to eliminate interference from sulfides. After cooling the solution is filtered into a 250 ml volumetric flask. The solution is brought up to the reference mark with distilled water. 50 ml. of this solution is withdrawn and placed in a flask along with 1 gram mercuric sulfate, 5 to 6 ml concentrated H_2SO_4 (SP. GR. 1.84), 1 gram of silver sulfate and 25 ml. of 0.25N $\text{K}_2\text{Cr}_2\text{O}_7$ is added. The flask is then connected to a condensor and 70 ml of concentrated H_2SO_4 is slowly added and the flask is refluxed under low flame for approximately $1\frac{1}{2}$ to 2 hours. After refluxing the solution is cooled, transferred into a 500 ml flask and diluted to 300 ml. After cooling to room temperature, 10 drops of ferrion indicator (1, 10 phenanthroline) are added and the solution is titrated to color change (green to red) with 0.25N ferrous ammonium sulfate solution. Water soluble organic matter is reported as follows:

$$\text{meq CrO}_4 - \text{meq Fe}^+ = \text{meq O}_2$$

$$\text{meq O}_2 \cdot 8 \cdot 1,000/50 = \text{ppm O}_2/1$$

The chemical oxygen demand (COD) of the sample as represented by water soluble organic material is reported as follows:

$$\text{COD/gm particulate} = \text{ppm O}_2/1 \cdot 5 \cdot 100/100 \cdot 30 \cdot 2$$

DETERMINATION OF SULFUR AS Na_2S

50 A 10 ml aliquot of the 500 ml solution derived from the filtration of the 30 gram particulate sample during carbon determination is introduced into a 500 ml flask, diluted with 100 ml distilled water and acidified with 1 normal HCl. The acidified solution is titrated with 0.1 N iodine with starch indicator. The results are reported as follows:

$$\text{Percent Na}_2\text{S} = 100 \cdot \text{Vol. of Iodine} \cdot 0.1 \cdot 0.039 \cdot 500/10 \text{ ml} \times 30.0 \text{ gms.}$$

Total oxygen demand of the sample, which is a convenient measure of activity of the additive of this invention is defined and determined as follows:

Total oxygen demand is the sum of the oxygen required to oxidize carbon to carbon dioxide, the amount of oxygen to oxidize sodium sulfide to sodium sulfate and the oxygen demand of the water soluble organics. The oxygen demand of carbon is determined by multiplying percent carbon by 32/12 while the oxygen de-

mand for sodium sulfide is determined by multiplying percent sodium sulfide by 64/78.

The results of the field test are summarized Table A below where sample 1 was taken about 20 minutes prior to treatment with the additive of this invention, and samples 2-6 were taken at 24 hour intervals after beginning treatment with the additive of this invention. Total oxygen demand is reported for each sample.

Table A

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Sample	Time/hrs.	%Na ₂ S	%C	COD/gm sample water soluble organics	Total oxygen demand
1	0	2.82	2.01	.57	8.22
2	24	.61	.43	.31	1.94
3	48	.32	.25	.17	1.10
4	72	.12	.37	.20	1.28
5	96	1.00	.24	.33	1.79
6	120	—	.65	.31	2.04

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The effect of the additive of this invention on the total oxygen demand of the particulate matter sampled just prior to and during the test period can be seen from the FIGURE where total oxygen demand of the samples of flue gas particulates is plotted against the time of taking the sample just before and after introduction of the additive of this invention as previously described.

It will be seen that within 24 hours after introduction of the additive there is a sharp decline in the total oxygen demand of the samples and that the total oxygen demand remains at a substantially low level throughout the period of treatment. The reduction in total oxygen demand undoubtedly occurs much sooner than is shown in the FIGURE since data was only taken on a twenty four hour basis. Observations made prior to and during the testing period confirmed that there was a reduction in deposit build-up and bridging in the superheater sections of the recover unit. The deposits formed were relatively softer and more friable while the additive was used and the soot blowers were more effective in removing soot during operation of the recovery unit when employing the additive than when no additive was employed.

The reduction in total oxygen demand is due to the presence of the catalyst metal which, by virtue of the additive of this invention, is present in effective amounts in the combustion zone because the additive is solubilized in the black liquor fuel. Likewise it will be seen that the additive is employed in economical amounts as distinguished from the prior art attempts to slurry catalyst metal oxides in the black liquor which required uneconomical amounts of metal oxide powders because of losses due to the insolubility of the powders in the black liquors. There was no adverse effect on the sulfidity balance of the recovery process indicating that the increased oxidation of carbon, sodium sulfide, and water soluble organics in the flue gas was not detrimental to the recovery process.

While the foregoing description has been concerned primarily with combustion of black liquor it should be clear to those skilled in the art that this invention is applicable to combustion of aqueous alkaline fuels from other processes which produce as combustion by-products a tenacious slag due to non-oxidation of carbon, and water soluble organics and other oxidizable products of the flue gas.

Unless otherwise specified, all percentages are ex-

pressed as percent by weight.

From the foregoing description it is readily apparent how the present invention accomplishes its various objectives. While the invention has been described and illustrated herewith with reference to certain preferred embodiments thereof, it is to be understood that it may be otherwise embodied within the scope of the appended claims.

I claim:

1. An aqueous alkaline fuel additive to reduce the detrimental effects of slagging encountered in the combustion of alkaline aqueous fuel, comprising an alkaline aqueous solution of a catalyst metal ion and a sequestering agent in sufficient quantity to maintain said catalyst metal ion in solution in an alkaline aqueous fuel, said catalyst metal being selected from the group consisting of manganese, copper, iron, tin, nickel, cobalt and mixtures thereof.

2. The fuel additive of claim 1 wherein said catalyst metal is manganese.

3. The fuel additive of claim 1 wherein said catalyst metal is manganese and iron.

4. The fuel additive of claim 1 having a pH of at least about 9.

5. The aqueous fuel additive of claim 1 having a total solids content of between about 25% to about 55%.

6. The fuel additive of claim 1 consisting essentially of:

Manganese acetate	5.82%
Sodium hydroxide	10.00%
Tartaric acid	15.75%
Water	68.24%

7. The fuel additive of claim 1 consisting essentially of:

Ferrous sulfate	3.8%
Manganese Sulfate	2.5%
Tartaric Acid	8.3%
Triethanolamine	21.2%
Tetra sodium ethylene dinitrilotetraacetate	8.2%
sodium hydroxide	11.9%
Water	44.1%

8. The aqueous fuel additive of claim 1 wherein said sequestering agent is present in amounts in excess of the stoichiometric amount required to maintain said catalyst metals in a soluble condition in an alkaline aqueous fuel.

9. A fuel additive for aqueous alkaline fuels to reduce the detrimental effects of slagging encountered in the combustion of said aqueous fuel, comprising a water soluble salt of a catalyst metal, a sequestering agent and the hydroxide of sodium or potassium in proportions to provide a pH of at least 9 when said additive is solubilized, the proportion of sequestering agent being at

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least the stoichiometric amount required to sequester the catalyst metal ion in an aqueous alkaline solution, said catalyst metal salt being selected from the water soluble salts of manganese, copper, iron, tin, nickel, cobalt and mixtures thereof.

10. The fuel additive of claim 9 wherein said catalyst metal salt is ferrous sulfate and manganese sulfate.

11. The fuel additive of claim 9 consisting essentially of on the dry weight basis:

Manganese acetate	18.4%
Tartaric acid	49.8%
Sodium Hydroxide	30.0%

12. The fuel additive of claim 9 consisting of on the dry weight basis:

Ferrous sulfate	6.8%
Manganese sulfate	4.5%
Tartaric Acid	14.9%
Triethanolamine	38.0%
Tetrasodium ethylenedinitrilo-tetraacetate	14.6%
Sodium Hydroxide	21.2%

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13. An alkaline aqueous fuel composition comprising a substantially uniform blend of a major amount of an alkaline aqueous fuel yielding upon combustion carbon and water soluble organics and a minor but effective amount, of a sequestered catalyst metal selected from the group consisting of manganese, copper, iron, tin, nickel, cobalt and mixtures thereof.

14. The fuel composition of claim 13 comprising from about 2 ppm to about 50 ppm of said catalyst metal.

15. The aqueous fuel composition of claim 13 comprising at least the stoichiometric amount of sequestering agent to sequester said catalyst metal ion for maintaining said catalyst metal ion in solution.

16. The fuel composition of claim 13 comprising an excess of sequestering agent over the stoichiometric amount to sequester said catalyst metal ion and maintain said catalyst metal ion in solution.

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