

Hydroxy- and Aminoethyl Imidazolines of Cottonseed Oil Fatty Acids as Additives for Diesel Fuels

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Abstract

In the research, aminoethyl imidazolines of cottonseed oil fatty acids with diethylenetriamine have been synthesized using the ultrasonic device creating the effect of cavitation. The yield of imidazolines was 90% - 95%. The influence of the synthesized imidazolines on lubricity quality of low sulfur diesel fuels having low lubricating quality was studied. The results showed that at concentrations 200 - 250 ppm the synthesized imidazolines can be applied as additives enhancing lubricity quality of diesel fuels.

Keywords

Cavitation, Imidazoline, Cottonseed Oil Fatty Acids, N-Hydroxyethyl Ethylenediamine, Diethylenetriamine

1. Introduction

Currently imidazolines and their derivatives are used as additives to diesel fuels, although it should be noted that works in this direction have just begun and need systematic studies [1]-[16].

Thus, in the work [7] the possibility of using an additive, containing (wt%) alkyl (C₃ - C₁₈) nitrate 75 - 90 by weight, anticorrosion component 5 - 15 by weight, a hydrocarbon fraction boiling in the range 120°C - 270°C to 100 wt%, was shown. Anticorrosive component is selected from the group consisting of 3, 4, 4-trimethyl-2-phenyl octane acid, 2-imidazoline, alkyl (C₄ - C₉) thiazolidine, N-oleilsarkozin. The additive may further contain

a copolymer based on ethylenically unsaturated monomers in an amount of 0.5 - 1.5 wt%. Diesel fuels based on the base fuel contain the above-described additive in an amount of 0.01 - 0.8 wt%. As the base fuel petroleum diesel fuel or gas condensate fuel may be used. The technical result is an improvement of anticorrosive properties and combustion quality, extension of storage life to 2 - 3 years, which is especially important in cold climates where condensation occurs and droplets of moisture favor the processes of hydrolysis and oxidation of fuels, thereby diesel fuels containing the known additives are prone to corrosion.

The use of the proposed additive in diesel fuels can not only improve the performance of petroleum and gas condensate diesel fuels, but also increase their storage life to 2 - 3 years compared with diesel fuels being used which have storage life of no more than 1 - 1.5 years.

As an additive reducing toxicity of exhaust gases and improving the smoke suppression properties of diesel fuels in the work [8] barium alkyl phenolate and the additive selected from the group: the reaction product of carboxylic acid with diethylenetriamine, the reaction product of sulfocarboxylic acid with diethylenetriamine, the reaction product of alkyl phenol with hexamethylenetetramine, diethylenetriamine and boric acid with the following ratio of components, wt%: barium alkyl phenolate 0.045 - 0.4; additive 0.005 - 0.1; diesel up to 100 were used.

In the patent [9] as a multifunctional additive, namely a demulsifier, corrosion inhibitor and/or an additive for lowering the pour point oxyalkylated fatty amines and fatty amine derivatives are used.

As is known, the increase of the efficiency of fuel combustion in the internal combustion engine increases the engine power, fuel economy, and reduces particulates in the exhaust gases. In order to achieve all of the above-mentioned parameters in [10] the additive containing the following components: di-tert-butyl peroxide, imidazoline of tall oil fatty acids and neodecanoic acid were used. In this composition, the organic di-tert-butyl peroxide is a source of supplemental oxygen and free radicals for acceleration of combustion chain reaction for the diesel fuel. Imidazolines of tall oil fatty acids act as an ashless detergent to maintain fuel system cleanliness (including combustion chamber and injector), absorb moisture, preventing rust and corrosion; neodecanoic acid acts as an initiator and stabilizer for the above-mentioned organic peroxide and provides resistance of diesel fuel to microbes which is also important when using biodiesel fuel.

Alkyl imidazolines with varying degrees of ethoxylation were studied as antioxidants of hydrocarbons of fuel fractions in the work [11]. It was found that while using the above-mentioned imidazolines the time of oxidation inhibition is approximately two times higher than when using the commercial oxidation inhibitor ZDDP.

In the present work the process of obtaining amino- and hydroxyethyl imidazolines of cottonseed oil fatty acids using ultrasonic cavitation has been investigated and the synthesized imidazolines were added to diesel fuels to improve their lubricity.

2. Materials and Methods

As initial reactants there were used N-hydroxyethyl ethylenediamine (HEEDA) produced by "Sigma Aldrich" company (Germany) and diethylenetriamine produced by "Merck" company (Germany). Physicochemical properties of the initial used reactants are listing in **Table 1**.

Table 1. Physicochemical properties of the used initial reactants.

Names of substances properties	N-hydroxyethyl ethylenediamine	Diethylenetriamine
Molecular formula	$C_4H_{12}N_2O$	$C_4H_{13}N_3$
Molecular mass, g/mol	104.2	113.2
Aggregate state	Viscous liquid	Liquid
Density at 20°C, g/s·m ³	1.03	0.95
Melting temperature, °C	-28	-35
Boiling temperature, °C	238 - 240	206 - 209
Color	Light yellow	Colorless
Degree of purity, %	99	99
Index of refraction (n_D)	1.4850	1.4826

The composition of a mixture of fatty acids obtained by hydrolysis of cottonseed oil was determined according to ASTM D 6584 on the chromatograph Agilent 78A (the capillary column Zebron ZB-5HT Inferno, active phase of 5% phenyl-95% dimethylpolysiloxane, 15 m × 0.32 mm × 10 μm, the carrier gas-nitrogen) and is shown in **Table 2**.

The elemental composition of the obtained imidazolines was determined using device “2400 CHN Elemental Analyzer” of “Perkin Elmer” Company.

As a source of ultrasonic vibrations there were used the ultrasonic processor UIP2000hd with the following specifications: COP > 85%, the operating frequency 1 - 20 kHz, range of operating amplitudes 40% - 100%, power consumption 200 - 240 V, AC frequency 48 - 63 Hz.

The synthesis of the above listed imidazolines was conducted by the following procedure: in a four-neck flask equipped with an ultrasonic sonotrode, a thermometer, a Dean-Stark trap and a dropping funnel the calculated amount of the amine dissolved in 100 ml of *o*-xylene is placed, the sonotrode is activated and the temperature of the mixture rises to the boiling point of *o*-xylene. Thereafter, through a dropping funnel during 20 - 25 minutes the calculated amount of fatty acid previously diluted with *o*-xylene is given to the flask.

Water released at the stage of amidoamine formation was distilled in a Dean-Stark trap as an azeotrope with *o*-xylene. Upon termination of water extraction system is connected to a vacuum pump and the reaction continues until release of water formed as a result of the formation of imidazoline rings stops. Upon completion of the synthesis a viscous liquid was formed at the bottom of the flask.

In the second stage, the effects of imidazolines of cottonseed oil fatty acids on lubricity of hydrorefined low sulfur diesel fuel have been studied. As a base diesel fuel two (D-I and D-II) diesel fuels subjected to hydro refining and significantly different from each other in some quality indicators have been used and their properties are shown in **Table 3**.

The influence of the mentioned imidazolines on lubricity of DI and D-II diesel fuels was investigated on HFRR apparatus according to the CEC F-06-A-96 method. In the tests the temperature was 60°C and the volume of used fuel samples was 2 ml. The effectiveness of the fuel lubricity was evaluated with photomicroscope by measurement of wear scar diameter (WSD) of balls.

3. Discussions and Conclusions

3.1. Synthesis of Fatty Acid Imidazolines

The mechanism of the imidazolines synthesis reaction is following.

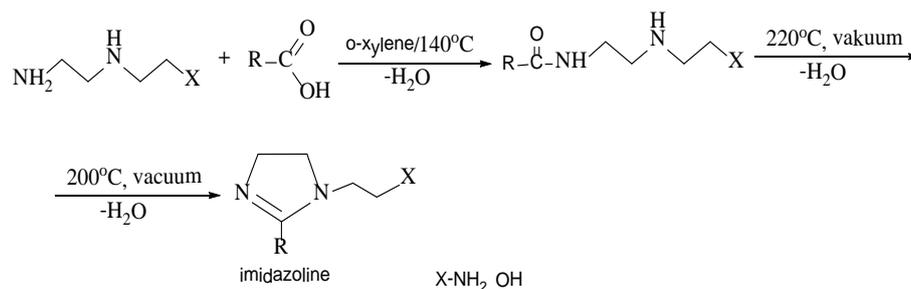


Table 2. Fatty acids of cottonseed oils.

Fatty acids	Content, % wt
Lauric (12:0)*	-
Myristic (14:0)	0.8
Palmitic (16:0)	22
Stearic (18:0)	2.5
Oleic (18:1)	30
Linoleic (18:2)	37.2
Linolenic (18:3)	7.5

Table 3. Physical and chemical properties of diesel fuels used in the research.

Indicators	Diesel fuels	
	D-I	D-II
Cetane number	47	46
Density, kg/m ³ at 20°C	849.5	851.0
Kinematic viscosity, mm ² /s at 20°C	2.23	2.29
Acidity, mg KOH/100s·m ³ fuel	0.01	0.06
Fractional composition, °C		
Boiling start	190	196
10% distillation temperature	210	215
50% distillation temperature	270	275
90% distillation temperature	335	345
96% distillation temperature	345	350
Ignition temperature, °C	73	74
Hydrocarbon composition, %		
Aromatic	21.23	25.92
Paraffin-Naphthene	78.52	72.38
Unsaturated	0.25	1.70
Total sulfur content, wt%	0.0012	0.0035
Freezing point, °C	-36	-35
Cloud point, °C	-28	-30
Amount of water, %	-	-
Lubricity, μm (average value)	620	601

It is assumed that in this method of synthesis the effect of cavitation created by ultrasound provides the equal distribution of free molecules in the entire volume of solvent by breaking the hydrogen bond between acid and amine molecules and thus increases the possibility of their encountering. In addition it is assumed that the effect of cavitation weakens bonds between atoms within molecules, which are one of the necessary conditions for speeding up the reaction. However, the research conducted has proven that after the certain amplitude value of ultrasound the decomposition of molecules leads to additional reactions in the reaction mixture, which is undesirable. Given this the synthesis process has been conducted at the various values of ultrasound amplitude, temperature, molar ratio of the starting materials and reaction time and as a result the optimal conditions with the highest yield of the reaction product (imidazoline) for these factors were found (Table 4).

These studies have revealed the possibility of obtaining N-(2-hydroxyethyl)- and N-(2-aminoethyl)-imidazolines of fatty acids of cottonseed oil under the influence of ultrasonic cavitation with 90.2% - 92.8% yield and a substantial reduction of reaction time compared to non-cavitation way of obtaining identical imidazolines from 12 - 22 hours to 4.5 - 5 hours.

The structure of the hydroxy- and aminoethyl imidazolines of fatty acids was confirmed by IR (500 - 3500 cm⁻¹, Bruker) and NMR (300 MHz, Bruker) spectroscopy.

In the ¹H NMR spectrum of N-(2-aminoethyl)-imidazolines of fatty acids of cottonseed oil protons of amine group of the imidazoline appear as a singlet of one proton at 1.64 - 1.67 ppm, protons of methylene groups in the moieties CH₂-NH₂, CH₂-N, N-CH₂ and CH₂N=C in the form of a triplet at 2.21 - 2.23, 3.33 - 3.36, 2.74 - 2.77 and 3.63 - 3.68 ppm respectively.

In the ¹³C NMR spectrum of the specified imidazoline the peak of the carbon atom in the moiety -N=CR-N- appears at 165.8 - 166.1 ppm, the peaks of the carbon atom of methylene groups of -CH₂-N=CR-moiety—at 50.7 ppm, CH₂-N=-moiety—at 52.7 - 53.5 ppm, =N-CH₂-moiety—at 54.4 - 55.2 ppm, and -CH₂-NH₂-moiety—at 41.6 - 43.7 ppm.

In the IR spectrum 2-stearin-N-(2-aminoethyl)imidazoline stretching vibrations of NH₂-group appear at 3289 s·m⁻¹, of C=N-group at 1637 s·m⁻¹.

Table 4. Yield of hydroxy- and aminoethyl imidazolines of fatty acids of cottonseed oil depending on the parameters of the process.

Symbol	Acid	Amine	Molar ratio acid:amine	Amplitude of ultrasonic vibrations %	Duration of reaction, hrs	Temperature of reaction, °C	Yield of imidazolines, %
FA-Im(NH ₂)	Fatty acid	DETA	1:1.5	50	4.5	200	90.2
FA-Im(OH)		HEED	1:1.5	50	4.5	200	91.8

3.2. The Study of N-(2-Hydroxyethyl)- and N-(2-Aminoethyl)-Imidazolines of Fatty Acids of Cottonseed Oil as Antiwear Additives to Diesel Fuels

In order to study the effects of FA-Im(OH)- and FA-Im(NH₂) imidazolines on lubricity quality of D-I and D-II diesel fuels, in the first place the lubrication effect of D-I and D-II diesel fuels in their pure state was tested. It was found that when using D-I and D-II diesel fuels the WSD was 620 and 601 μm respectively. The results show that, in fact, A-I and A-II diesel fuels do not meet the requirements for lubricity quality of modern diesel fuels (WSD ≤ 460 μm).

In order to study the influence of FA-Im(OH)- and FA-Im(NH₂) imidazolines on lubricity quality of D-I and D-II low sulfur diesel fuels the WSD for D-I and D-II diesel fuels was determined after adding imidazolines to diesel fuels at 50 - 300 ppm. The WSD for each concentration was measured three times and eventually the average value of WSD was taken.

The curves of WSD dependence on concentration of imidazolines for D-I diesel fuel obtained from adding FA-Im(OH) and FA-Im(NH₂) imidazolines to D-I and D-II diesel fuels are given in **Figure 1**.

As shown on **Figure 1**, the lubricity of D-I diesel fuel rises with the increase of imidazolines concentration in it. Thus, when concentration of FA-Im(OH) and FA-Im(NH₂) imidazolines in the diesel fuel is 50 ppm the WSD is 600 μm and 595 μm respectively. When increasing the concentration from 50 ppm to 250 ppm the WSD for FA-Im(OH) imidazoline and FA-Im(NH₂) imidazolines decreases to 474 μm and to 465 μm respectively. As seen from the results, the WSD values for FA-Im(OH) imidazoline at concentration of 300 ppm and for FA-Im(NH₂) imidazoline at concentration of 300 ppm in D-I diesel fuel are less than 460 μm. This shows that at the indicated concentrations of imidazolines D-I diesel fuel meets the requirements for lubricity placed on modern diesel fuels. In addition, at concentration of FA-Im(OH) and FA-Im(NH₂) higher than 300 ppm and 250 ppm respectively, no significant changes were observed in the lubricity quality of D-I diesel fuel. Therefore, the indicated concentrations can be considered as the optimal concentrations allowing to improve lubricity quality of D-I diesel fuel in accordance with modern quality standards.

In the research work, the effects of FA-Im(OH)- and FA-Im(NH₂) imidazolines on lubricity quality of D-II low sulfur diesel fuel were also studied.

In **Figure 2** the curves of WSD dependence on concentration of imidazolines have been given for D-II diesel fuel with added FA-Im(OH)- and FA-Im(NH₂) imidazolines.

As shown on **Figure 2**, similar to D-I diesel fuel with the increase of concentrations of FA-Im(OH) and FA-Im(NH₂) in D-II diesel fuel the lubricity quality of the diesel fuel rises. Thus, when increasing the concentration of FA-Im(OH)- and FA-Im(NH₂) in D-II diesel fuel from 50 ppm to 250 ppm the WSD for FA-Im(OH) and FA-Im(NH₂) decreases from 585 μm to 463 μm and from 577 μm to 454 μm, respectively. As can be seen from the results, the optimal concentrations of FA-Im(OH) and FA-Im(NH₂) in D-II diesel fuel are 300 and 250 ppm, respectively. Thus, in concentration of FA-Im(OH)-imidazoline 300 ppm and concentration of FA-Im(NH₂) 250 ppm in D-II diesel fuel the WSD value is lower than the modern requirement (460 μm).

According to the results obtained it can be noted that by applying the effect of cavitation created by ultrasound to the classical method of imidazolines synthesis the reduction of synthesis duration 2 - 5 times compared to other methods of synthesis and the yield of imidazolines 92% - 97% can be achieved. On the other hand, the comparison of the effect of FA-Im(OH) and FA-Im(NH₂) on lubricity of both diesel fuels shows that compared to FA-Im(OH) the effect of FA-Im(NH₂) imidazoline on lubricity of diesel fuels is higher. The reason for this can be given that because of the lower electronegativity of nitrogen atom compared to oxygen atom electrons in the amino group can easily form bonds with rubbed surfaces at the expense of electron gas.

This causes the recovery of the layer destroyed in the process of friction in a short period of time and thus rubbed surfaces wear away in a less degree.

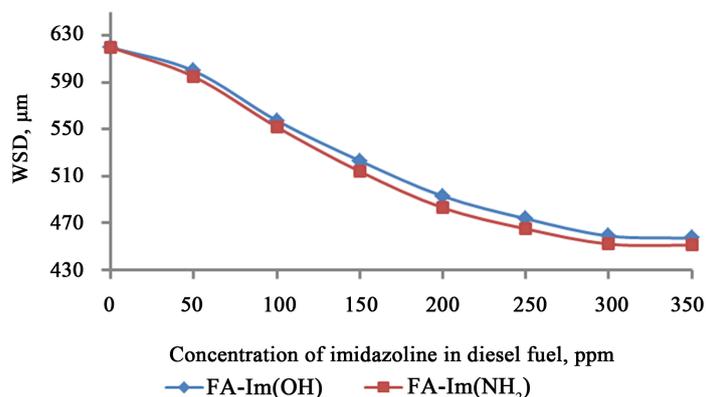


Figure 1. The effect of FA-Im(OH) and FA-Im(NH₂) imidazolines on lubricity quality of D-I diesel fuel.

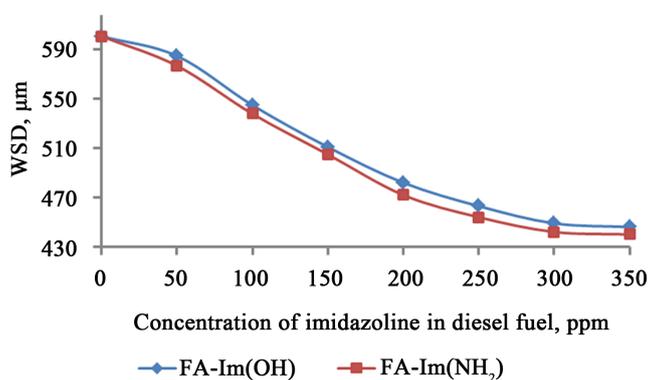


Figure 2. The effect of FA-Im(OH) and FA-Im(NH₂) imidazolines on lubricity quality of D-II diesel fuel.

In addition, according to the curves in **Figure 1** and **Figure 2**, very insignificant differences between them are observed. This shows that the application of imidazolines to diesel fuel as lubricity-enhancing additives depends insignificantly on the hydrocarbon composition of diesel fuel.

Finally, it should be noted that FA-Im(OH) and FA-Im(NH₂) imidazolines can be used as additives enhancing the lubricity of diesel fuels.

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