A- INTRODUCTION OF THESIS

1. The urgency of the thesis

Facing the risk of fossil fuel resources gradually depleted and the challenges of increasing enviromental pollution caused by exhaust fumes from transportation vehicles, besides finding new and clean energy resources, many countries are looking for solutions to save fuel and reducing pollution emissions from engines. In parellel with the study and development of solutions to improve “hardware” of engines, the study direction of using elmusion fuels and saving fuel, reducing pollution emissions additives has been paying attention to.

Emulsion diesel fuel is a fuel in which water is dispersed in the form of emulsified particles ranging in size from micrometers to nanometers. Diesel fuel-saving additives usually include water in oil emulsifiers and fuel saving additives based on metal oxide nanoparticles.

In recent years, the strong development of nanotechnologies has contributed to promoting the development of many related sciences, especially fuel additives. Fuel additives based on nanotechnologies usually have high technical and economic efficiency. A small amount of nano-additives can significant improve fuel economy and emission reductions.

On that basis, this phD thesis topic focuses on studying the preparation and investigating the activity of the new generation nanoemulsion additive, saving fuel and reducing emissions for diesel engines, through the study of the preparation of nanoemulsions. Surfactants have the ability to disperse the active ingredients of the additive in the fuel to the size of nanometers in the fuel, thereby enhancing the effectiveness of the additive.

With this approach, it can be said that the thesis topic that the PhD student has chosen is topical, has scientific significance and has practical applicability.

2. Research objectives and content of the thesis

The main objective of the thesis is "Study on synthesis and efficiencies of the new nanoemulsion additives for the DO fuel".

The thesis was carried out under the scientific guidance of Prof. Dr. Vu Thi Thu Ha.

To achieve the goal, the thesis has done the following contents:

- ✓ Research and prepare quality surfactants/surfactants systems as raw materials for making nano-emulsions;
- ✓ Research on preparation of new generation nanoemulsion fuel additives for diesel engines;
- ✓ Research and evaluate the properties of additives and fuel additives;
- ✓ Research and test new generation nanoemulsion additives on laboratory benches and field test;
- ✓ Study and propose the mechanism of the new generation nanoemulsion additive;

3. Scientific and practical significance of the thesis

Scientifically, the thesis has made certain contributions to the research on synthesis and application of non-ionic surfactants in the preparation of new generation nanoemulsions additives.

The ability to apply additives to reduce fuel consumption, increase engine power, reduce harmful emissions at the ratio of mixing with fuel as small as 1/8,000 (v.v.) when using the new generation nanoemulsion additives for vehicles and equipment using diesel fuel.

4. New contributions of the thesis

✓ The surfactant compounds suitable for making new generation nanoemulsions had been successfully synthesized, including: Synthesis of ethoxylated coconut oil diethanolamide surfactant containing ethylene oxide groups in the range of 8. HLB value range of the product is 6 - 8; Synthesis of fatty acid hydroxyethyl imidazoline surfactant from tall oil, with HLB range from 8-10; Synthesis of polyethylene glycol ester (PEG) of fatty acids by trans-esterification between methyl oleate and polyethylene glycol using MgO and hydrotalcite catalysts. This surfactant has the ability to stabilize the nanoemulsion system in the reverse nanoemulsion additive when combined with the 2 surfactants prepared above.

✓ The new generation nanoemulsion additives had been successfully prepared including water-in-oil nanoemulsions dispersed at the nanoscale using a mixture of 3 surfactants (ethoxylated coconut oil diethanolamide, hydroxyethyl imidazoline and PEG) and high power ultrasonic dispersion method and nano iron oxide nanoemulsion additives composition, with nanoemulsion additives/nano iron oxide nanoemulsion additives ratio of 4/1 v.v.. New generation nanoelmusion additives for DO fuel efficiency on the bench test is 5.1% at full load and CO emissions reduction is 10.76%, HC reaches 11.46%, NO_x reaches 11.19% and PM reaches 5.52%, according to the ECER 49 test cycle at a low mixing ratio of 1/8,000 by volume with a fuel nanoemulsion particle size of 2-4 nm, without affecting the basic properties of the fuel according to TCVN 5689:2018 and parts in direct contact with the fuel of the engine.

✓ The mechanism of action of the new generation nanoemulsion additives had been proposed based on the combination of micro-explosion and heterogeneous nanocatalysts in enhancing the combustion efficiency of diesel fuel, reducing harmful gas emissions and soots.

5. The structure of the thesis

The thesis consists of 142 pages excluding the List of abbreviations, figures and tables, 43 tables, 65 drawings and graphs, distributed into sections including: Introduction - 3 pages; Overview - 36 pages; Experiments and research methods - 21 pages; Results and discussion - 65 pages; Conclusion - 2 pages; New points of the thesis - 1 pages, List of published works - 2 pages; References - 12 pages (122 references).

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B – MAIN CONTENTS OF THE THESIS

Chapter 1: OVERVIEW

Currently, the strong development of nanotechnology contributes to promoting the development of many related sciences, especially fuel additives. The additive manufacturing technology is also significantly improved when nanotechnology is applied. Fuel additives based on nanotechnology bring high technical and economic efficiency. A small amount of nano-additives can bring about significant fuel economy and emission reductions. The application of nanotechnology in additive manufacturing promises the ability to solve many problems that have existed since before nanotechnology was appeared.

Diesel fuel emulsion and fuel-saving and emission-reducing additives are effective measures to improve combustion efficiency in diesel engines leading to fuel savings and reduction of harmful gas emissions;

Emulsion diesel fuel is a fuel in which water is dispersed in the form of emulsified particles with sizes ranging from micrometers to nanometers; Fuel-saving additives for diesel usually include water-in-oil emulsifiers and fuel-saving additives based on metal oxide nanoparticles;

Surfactants used in the preparation of fuel emulsions or micro-emulsions are usually non-ionic surfactants such as ethoxylated alkanolamide compounds from animal and vegetable fats and oils and surfactants based on amidoamine derivatives from vegetable fats and oils. and polyamines. In Vietnam, there are several groups of authors who have studied the synthesis of surfactants for the emulsification process in general. However, there have been no studies to synthesize the family of surfactants based on ethoxylation of alkanolamides from animal fats and vegetable oils and surfactants on the basis of amidoamine derivatives from animal fats and vegetable oils and polyamines, for application in Fabrication of water-in-oil micro-emulsions with emulsion particle size of several nm, with high stability.

There have been many studies on the preparation and application of emulsion diesel fuel. However, there has not been any systematic and comprehensive study from the preparation of surfactants to meet the requirements of nanoemulsion systems, additive preparation, fuel additive preparation, to the evaluation of effects. Effects of additive-phase fuel on safety in operation, storage, transportation, assessment of fuel efficiency and emission reduction.

In general, each research work only focuses on one aspect of the problem while in order to be able to put an additive into a wide application, it is necessary to pay attention to all aspects, economic, technical, environment, fire safety. In particular, there are almost no studies on the effects of additives or directly of surfactants on the plastic content in the fuel, the influence of the active substances on the operating safety of the engine. (The creation of plastic can lead to clogging of nozzles, filters, etc.). Moreover, most of the works use a large amount of additives to mix with diesel (sometimes up to nearly 1% by volume);

There are many research works on fuel-saving additives based on metal oxide nanoparticles for gasoline fuel. However, there are very few studies systematically and methodically on diesel fuel-saving additives based on metal oxide nanoparticles while the demand for diesel fuel saving and emission reduction from diesel engines is also very high. high, not inferior to the demand for gasoline fuel.

Therefore, the research and development of the new generation nanoemulsion fuel additives for diesel engines to reduce fuel consumption and harmful emissions, systematically and comprehensively, is urgent and science and practice meanful.

Chapter 2: EXPERIMENTS

2.1. Chemicals, tools and equipment

The chemicals are sourced from chemical suppliers such as Sigma Aldrich, Merck, China and Vietnam. The thesis uses specialized equipment such as transducer ultrasonic vibrating devices, etc..

2.2. Synthesis of surfactants for use in nanoemulsions

2.1.1. Synthesis of non-ionic surfactants on the basis of ethoxylation of alkanolamides from animal fats and vegetable oils

Synthesis of alkanolamides

Alkanolamide was prepared by amideation reaction between diethanolamine and methyl ester of vegetable oil at 154^{o}C for 6 hours, split products phases, purified with cold ethyl acetate, washed with distilled water to neutral, dried in a vacuum oven, according to the reaction equation:

$RCOOCH_3 + NH(CH_2CH_2OH)_2 \rightarrow CH_3OH + RCON(CH_2CH_2OH)_2$

Ethoxylation of alkanolamide

Alkanoamide was ethoxylated by adding alkanolamide and KOH to the autoclave, reacting with ethylene oxide gas at 160^{o}C, catalyzed neutralization with HCl solution, purified with isopropanol, according to the reaction equation:

$RCON(CH_2CH_2OH)_2 + CH_2CH_2O \rightarrow RCON(CH_2CH_2O)_{n+1}H$

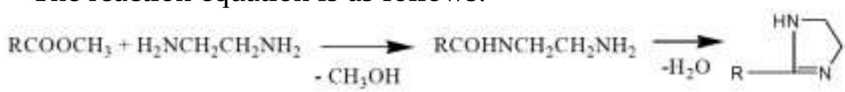
2.2.2. Method of synthesizing surfactants based on amidoamine derivatives

Synthesis of imidazoline

The synthesis of imidazoline goes through 2 stages: synthesis of amidoamine and synthesis of imidazoline from the resulting amidoamine. Amidoamine is synthesized by reacting the methyl ester with ethylendiamine at 135^{o}C for 5 hours, distilling the excess ethylendiamine at 116^{o}C, purified with ethyl acetate.

After that, the resulting amidoamine product is put into a heating vessel at low pressure, at 250^{o}C, then purified with hot ethyl acetate, the filtrate is cooled to crystallize, collect and dry the resulting solid.

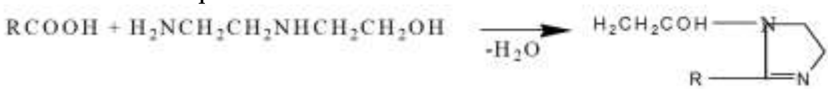
The reaction equation is as follows:



Synthesis of hydroxyethyl imidazoline

Tall oil fatty acids and N-(2-Hydroxyethyl)ethylenediamine react at 140°C for 6 h. Then reduce the pressure (5 mmHg) raise the temperature to 250^{o}C for 2 hours. Purified with ethyl acetate, the product is obtained in the lower layer.

The reaction equation is as follows:



2.2.3. Synthesis of surfactants on the basis of esters of polyethylene glycol with fatty acids

Methyl ester of coconut oil is reacted with polyethylene glycol and heated to 200^oC, with MgO catalyst added, and maintained at 200^oC for 2 hours. Filter the catalyst, wash with hot saturated brine, separate the organic phase, and dry the product.

The reaction equation is as follows:

$$RCOOCH_3 + HO(CH_2CH_2O)_nH \xrightarrow[-CH_3OH]{} RCOO(CH_2CH_2O)_nH$$

2.3. Preparation of new generation nanoemulsion fuel additives for diesel engines

Preparation of water-in-oil nanoemulsions

Mixtures of ethoxylated coconut oil diethanolamide/hydroxyethyl imidazoline/polyethylene glycol ester in the ratio 3/2/1 by weight, into a beaker containing 290 g tall oil,80 g n-butanol and 15 g Span-80 , stirring at 120 rpm, collect. transparent mixture. Keep the mixture stable for 15 minutes. Add 100 g H_2O, sonication at 20 kHz for 90s, sonication power 200 W. Finally, add 20 g of 28% NH_3 solution. The resulting nanoemulsion is transparent and unseparated, when observed with the naked eye.

Preparation and preparation of nanoemulsion additives containing iron oxide nano

The mixture of Triton-X and n-hexanol was added to the diesel fractionated hydrocarbon mixture then separated into two equal parts, one part was added with $FeCl_3$ solution, the other part was added with NH_3 solution. Then slowly add the part containing the iron salt into the NH_3. Then add n-butanol (1/1 v.v.).

Preparation of the new generation nanoemulsion additives combination

Mixing water-in-oil nanoemulsions and nano iron oxide containing nanoemulsions in a volume ratio of 4/1 to obtain the new generation nanoemulsion additives.

2.4. Product quality assessment

The product quality of the synthesized samples was structurally characterized by IR, MS, HPLC, NMR methods.

Experimental determination of HLB, determination of color and other analyzes of the product was carried out at KEYLAB PRT. Particle size distribution range, measured on a Zetasizer nano ZS at the Institute of Materials Science, Vietnam Academy of Science and Technology by DLS method.

The quality of diesel fuel and diesel fuel with additives is assessed according to the standard TCVN 5689: 2013

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2.5. Evaluation of the compatibility of additive phase fuels for components in direct contact with fuel in diesel engines

The test components are selected from the parts of the PE IFA TGL 12 378 such as high-pressure pump and some components made of non-metallic materials, such as high pressure pump gasket.

2.6. Efficiency test of additive fuel on bench test

Conducted evaluation of the efficiency of the new generation nanoemulsion additives blended fuel, according to the recommended phase-by-volume ratio of 1/8,000, the test fuels met TCVN 5689:2018, according to the standard test methods. or test control method. These tests were carried out at the Research Center for Engines, Fuels and Emissions, School Of Transportation Engineering - Hanoi University of Science and Technology (Figure 2.1).

Figure 2.1. Test engine on bench test

For the new generation microemulsion additives, the test engine is Hyundai D4DB engine (Korea).

Table 2.1. D4DB engine specifics

Model		Hyundai D4DB
Displacement (cc)		3.907
Bore x stroke (mm)		104 x 105
Maximum power (Hp/rpm)		130/2.900
Maximum torque (kg.m/rpm)		37/1.600
Dimensions (mm)	Length	815
	Width	695
	Height	765,5
Weight in dry (kg)		350
Engine type (stroke)		4
Number of cylinder		4
Cylinder arrangement		In-line
Firing order		1 - 3 - 4 - 2
Compression ratio		18:1

Test the engine control method with fuel samples according to the following basic steps:

- Check and calibrate test equipment;
- Run the engine stably for 3 hours with 200Nm running mode, corresponding to 70% of the load before measurement;
- Stabilize coolant temperature, lubricating oil temperature and fuel temperature;
- Measure the engine characteristics according to the external characteristic curve (100% load). At points on the external characteristic curve, the amount of fuel supplied for one cycle, gct, is constant when tested with different fuels;
- Measure the fuel consumption and emission components according to the load curve at a specified rpm, with each torque change rate 10%, 25%, 50%, 75% and 100% respectively. load. The torques at the respective points on the load curve are kept the same when testing with different fuels (g_{ct} varies depending on the combustion efficiency of the fuel);
- Measure emission components at idle-mode.
- Evaluation of the test results of the engine's power, fuel consumption and emissions with each fuel pair.

2.7. Field test

The field test was carried out at Trang Kenh Limestone Mining Workshop - Vicem Hai Phong Cement Company according to the control method on trucks in static and dynamic modes to evaluate the effectiveness of next-generation microemulsion additives. new under actual operating conditions. The test subjects are 02 CAT 769D trucks using CAT 3408E engine, this is a dump truck of Caterpillar (USA) often used as a means of transport on construction sites and mining sites. The test fuels are commercial DO oil and new generation microemulsion additives blended DO in a volume ratio of 1/8,000. Fuel consumption is compared in the static mode and dynamic mode. The test procedure for measuring fuel consumption in static mode and dynamic mode is described in Figure 2.2.

The test was conducted with vehicles using diesel fuel without additives first, and then switching to diesel fuel with additives. During a fuel change, the non-additive fuel is drained, the additive fuel is filled in, and then the engine is run at idle for 30 minutes before performing the additive phase fuel test.

Loading and unloading side yards were created to increase the similarity in transportation trips, and testing was carried out for 2 vehicles to increase objectivity. Selected surveys with similar conditions as a basis for control/comparison. Eliminate statistics in surveys with incidents that cause loss of similarity during the testing process: car with broken parts, car with broken tire, car without air conditioning, unstable technical condition of vehicle, driver, etc. Unusual health vehicles, zigzag cars jostling, local traffic jams, etc., sudden rain and wind.

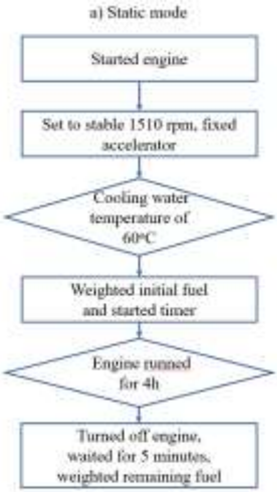

Figure 2.2. Test procedure to determine fuel consumption

For each test fuel, emissions will be measured at the top of each vehicle's chimney. Take at least 3 values of stable CO and NOX concentrations at idling modes at different engine rpm. For HSU % smoke, the measured value is determined at the maximum rpm.

Chapter 3: RESULTS AND DISCUSSION

3.1. Research on the preparation of surfactants

3.1.1. Study on preparation of surfactant based on ethoxylation of alkanolamide from animal fats and vegetable oils

The study used the Behnken Box model, with the help of Modde 5.0 software to optimize the experiment and determined the conditions for synthesizing alkanoamide from coconut oil as follows:

A mixture of diethanolamine and methyl esters of coconut oil, with a molar ratio of amine:ester = 1.6 in a three-necked flask equipped with a magnetic stirrer, condenser and thermometer, was heated to 154^{o}C under the condition of regenerating. stored, stirred at 500 rpm and kept at this temperature for 6 h. Then, transfer the mixture to a separating funnel and let it settle for one hour. After the reaction, the mixture splits into two sublayers. The upper layer is pale, containing mostly residual methyl laurate. The lower layer is dark in color, containing mostly product. Separate the 2 sublayers and wash the lower sublayer with cold ethyl acetate (0 - 5^{o}C) 5 times. The obtained products were dried at 70^{o}C under vacuum for 6 hours. Process efficiency reached 91%.

This thesis has determined the suitable conditions of the reaction to prepare ethoxylated coconut oil diethanolamide surfactant from coconut oil diethanolamide and ethylene oxide, to be used as raw materials for the preparation of nanoelmusion additives, which can be summarized as follows:

- Reaction temperature: 160^{o}C;
- Molar ratio of amide:ethylene oxide=10
- Reaction time: 60 minutes;
- Purification: The reaction mixture is neutralized with 0.01M HCl solution, then the product is extracted using isopropanol extraction solvent, with the ratio of 20 ml of solvent / 10g of product. The extraction process was repeated 2 times. The isopropanol excess contains the product that is separated and distilled at 82.6°C to recover isopropanol. The obtained product was dried at 105^{o}C to remove water stains.

The LC and MS spectra of the ethoxylated sample are presented in Figures 3.1 and 3.2.

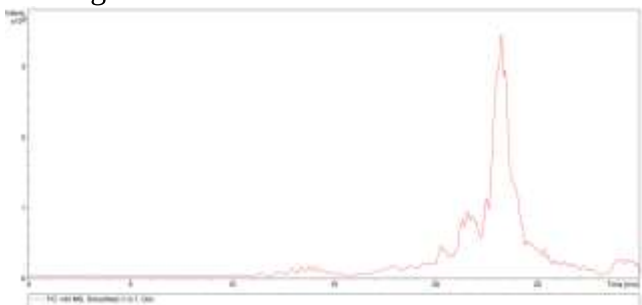

Figure 3.1. Spectrum LC product sample diethanolamide ethoxylated coconut oil

We see on the MS spectrum of the product sample, there are many peaks with a mass jump of 44 - 44.1, which is typical for the CH2CH2O fragment. The molecular ion pic m/e at 274.1 is typical for the fragment $RCON(CH_2CH2)_2$. From the MS spectrum, it can be seen that the ethoxylation product with the number of ethylene oxide units (n + m) from 1 to 16, in which mainly the ethoxylation product with the number of ethylene oxide units from 7 to 10.

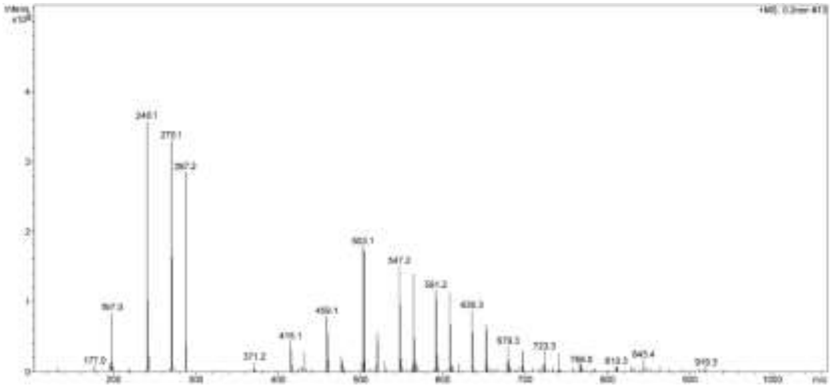

Figure 3.2. Spectrum MS product sample diethanolamide ethoxylated coconut oil

Do it this way, the reaction got over 91% product efficiency. The content of ethoxylated coconut oil diethanolamide in the product reaches over 99%. The resulting ethoxylation product contains an ethylene oxide group number from 1 to 16 (concentration in the range of 8). The HLB value range of the product is 6-8. With such properties and composition, the surfactant product is suitable for the preparation of nanoemulsion additives.

3.1.2. Research on the preparation of surfactants based on amidoamine derivatives from animal fats and vegetable oils and polyamines

This thesis used the Behnken Box model, with the help of Modde 5.0 software to optimize the experiment and determined the conditions for the synthesis of amidoamine, the results of the experimental preparation of the nanoemulsion additive system using the surfactant. imidazoline showed that the resulting mixture was cloudy. This shows that the synthetic surfactant imidazoline is incompatible with other components in the additive system. Therefore, it is necessary to synthesize imidazoline derivatives to increase the hydrophilicity of this surfactant. Among the derivatives of amidoamine, hydroxyethyl imidazoline contains an imidazoline ring and also contains an additional OH functional group, promising higher hydrophilicity than imidazoline without the substituent. Moreover, this surfactant can be synthesized directly from fatty acids without having to be converted to fatty acid methyl esters. This thesis has determined suitable conditions for the synthesis of hydroxyethyl imidazoline, as summarized below.

- Molar ratio of amine:acid = 1.8
- Stage 1: 140^{o}C, 6 hours;
- Temperature stage 2: 250^{o}C, 5 mmHg, 2 hours;
- Purification with ethyl acetate solvent at the rate of 20 ml of solvent /10 g of product, number of times of purification: 2 times. Dry at 70^{o}C in a vacuum oven, for 2-3 hours to collect the product.

Followed in this way, a yellow-brown product with the characteristic properties of the compound hydroxyethyl imidazoline is obtained. Efficiency is over 92%.

The 1H NMR spectrum of the product presented in Figure 3.3 shows peaks with σ = 0.838 - 0.865 ppm, representing the H of the CH3 group in the acid radical (R); the peaks with σ = 1.176 - 2.021 ppm characterize the H-bonded C no of the radical R ; the peaks with σ = 2.088 – 2.507 ppm characterize the unsaturated C-bonded H of the R radical; the peaks with σ = 2.601 – 2.627 ppm represent the H bound to C2; the peaks with σ = 2.974 – 3.000 ppm are typical for H bound to C3; the peaks with σ = 3.145 - 3.183 ppm characterize the H bound to C1; The peaks with σ = 3.434 - 3.473 ppm are typical for H bound to C4.

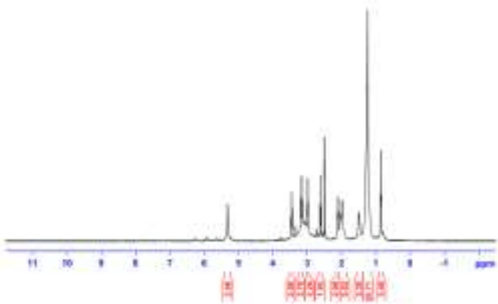

Figure 3.3. ^{1}H NMR spectrum of product sample hydroxyethyl imidazoline

The ^{13}C NMR spectrum of the product is presented in Figure 3.4. It is observed on the spectrum that the peak of C5 appears at σ = 166.41 ppm; the peak of the unsaturated Cs in the original R appeared at σ = 125.56 - 129.67 ppm; the peak of C1 appears at σ = 51.54 ppm; the peaks of C¬2, C3 and C4 appear at σ = 49.86 ppm, 49.76 ppm and 39.0 - 40.41 ppm; the peaks of the C_s in the R-group appeared at = 13.85 ppm, 21.91-22.03 ppm and 25.16 - 31.22 ppm.

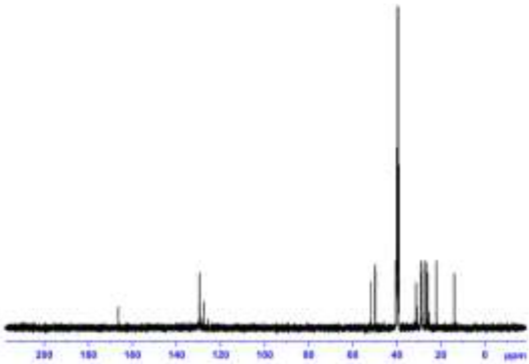

Figure 3.4. ^{13}C NMR spectrum of product sample hydroxyethyl imidazoline

On the IR spectrum of the hydroxyethyl imidazoline product (Figure 3.5), there is a peak at 3,261.63 cm^{-1}, representing the oscillation of the hydroxylethyl OH bond. The C=N bond has a characteristic peak at 1,610.56 cm^{-1}.

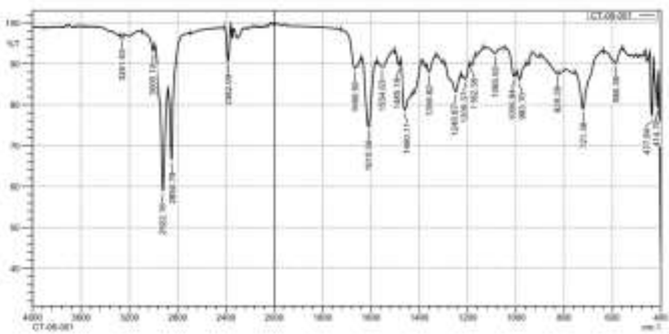

Figure 3.5. IR spectra of product hydroxyethyl imidazoline

The above characteristic results allow the conclusion that the composite product has the expected structure. The MS spectrum of the hydroxyethyl imidazoline product sample is presented in Figure 3.6.

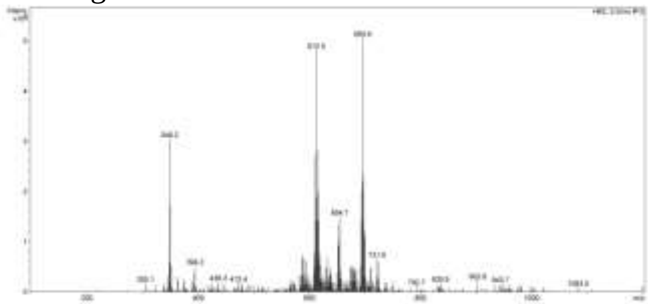

Figure 3.6. MS spectra of product hydroxyethyl imidazoline

The total amine content of some samples was determined according to ASTM D2073-92, showing that the optimal sample had an average total amine content of 151 mg/g.

Even so, the efficiency of water emulsification in DO fuel of the nanoemulsion additive, which is prepared from either of the two surfactants mentioned above, is not really high, as shown by the relatively high emulsion particle size, right after when mixing additives with fuel, as well as when storing fuel with additives after one month. This result suggests that it is necessary to increase the hydrophilicity of the additive system, specifically the need to add hydrophilic surfactants to the additive composition.

Considering that polyethylene glycol esters of fatty acids are a group of surfactants with wide applications, are environmentally friendly and can meet the technical requirements, the method of preparing this surfactant has been studied. Based on the survey results, it can be seen that the combination of these 3 surfactants significantly reduces the particle size of the water-in-DO oil emulsion, at the time of mixing as well as after one month of storage. It is noteworthy that the additive sample used a mixture of ethoxylated surfactants from coconut oil/hydroxyethyl imidazoline/PEG 400 esters, according to the weight fraction ratio 3/2/1, to create emulsions of less than 2 nm in size. Obviously, the addition of PEG 400 ester component is reasonable and brings significant effects in the preparation of nanoemulsions

3.2. Research on preparation of new generation nanoemulsion fuel additives for diesel engines

3.2.1. Research on the preparation of water-in-oil nanoemulsions

From the obtained results, this thesis proposes the preparation process by ultrasonic transducer method as follows:

Using the oil phase is tall oil, the main surfactant used is a mixture of ethoxylated coconut oil diethanolamide / Hydroxyethyl imidazoline / polyethylene glycol ester in the ratio 3/2/1 with a ratio of 10.3%, water content is 20%. The ultrasonic dispersion step was performed after the addition of water to the mixture and before the addition of NH_3 solution, under 200W ultrasonic conditions at 20 kHz for 90 seconds.

3.2.2. Research on preparation of nanoemulsion additives containing nano metal oxide

Research results on the preparation of nanoemulsions containing metal oxide nanoemulsions, on the basis of inheriting the additive preparation method of TD laboratory are as follows: Mix 156 g Triton X-100 and 102 g n-hexanol into the mixture diesel fractionated hydrocarbon, forming an oil phase with a volume of 1,000 L, stirring at 200 rpm, for 15 minutes. Divide the above mixture into 2 equal parts, store in two 2,000 ml beakers. The first volume fraction was mixed with 20 mL of 1 M $FeCl_3$ solution. The second volume fraction was mixed with 20 mL of 28% NH_3 solution. Stir the two mixtures on a magnetic stirrer at 200 rpm for 10 minutes until two transparent nanoemulsions are obtained. Slowly add the emulsion of iron salts to the nanoemulsion of NH_3, stirring at 200 rpm until the mixture is transparent.

The nanoemulsion system was left to stabilize for 5 hours. 1,000 mL of the nanoemulsion prepared above and 1,000 mL of 99% n-butanol were added to a 5,000 mL beaker and mixed with a boom stirrer at about 200 rpm, stirring time for 10 minutes. The size of the water-in-oil emulsion particles of the nano metal oxide -containing nanoemulsion admixture is nearly 70 nm.

3.2.3. Compatibility of mixtures of nano metal oxide containing nanoemulsions and water-in-oil nanoemulsions

Nanoemulsion additives containing nano metal oxides were investigated and mixed with water-in-oil nanoemulsions at different ratios to investigate the effects of mixing on the appearance of the mixture of both additives. At the mixing ratio of 1/4, the two additives are completely compatible and have high preservation durability.

The combination of the two additive systems still gives the average water-in-oil emulsion particle size that is almost equivalent to that of the water-in-oil nanoemulsion additive sample at the mixing ratio of 1/8,000 by volume. The resulting product is the new generation nanoemulsion additives. The new generation nanoemulsion additives has the basic properties listed in Table 3.1.

Table 3.1. Properties of new generation nanoelmulsion additives

N^o	Property	Unit	Method	Result
1	Closed cup flashing	^oC	TCVN 2693:2007	73,0
2	Viscosity at 40^oC	mm^2/s	TCVN 3171:2011	42,13
3	Copper strip corrosion test	-	TCVN 2694:2007	1b
4	Density at 15^oC	kg/m^3	TCVN 6594:2007	927,2
5	Appearance	-	TCVN 7759:2008	Red-brown color, transparent

At the ratio of mixing with diesel fuel 1/8,000, the additive does not significantly affect the criteria according to TCVN 5689:2018, while the Fe-Mn content and the actual plastic content of the fuel. The determined average size of water-in-oil emulsion particles by DLS method is 3 nm.

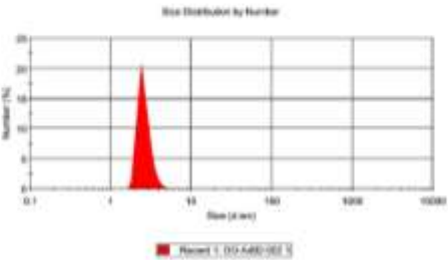

Figure 3.7. Size distribution range of water emulsion particles in new generation nanoemulsion additives phase fuel samples (dispensing ratio by volume 1/8,000)

Figure 3.8. Samples of component additives: nano iron oxide nanoemulsion additive (a), water-in-oil nanoemulsion additive (b) and new generation nanoemulsion additives (c)

3.4.4. Studying the effects of fuel additives on fuel contact parts

The research results in this Thesis for metal and non-metallic parts in direct contact with fuel in Diesel engines show the impact of fuel with additive blended and base fuel when start of the test and after the end of the test are similar (Figures 3.9, 3.10 and Table 3.2).

Table 3.2. Mass variation of the studied samples

N°	Parts	Desc.	Non-additive fuel			Additive blended fuel		
			Day 0	After 60 days	%	Day 0	After 60 days	%
1	Piston of high pressure pump	Alloy	40,2848	40,2847	-0,00	40,2652	40,2654	+0,00
2	Sealing Gasket	Synthet	6,7169	6,7218	+0,073	7,0304	7,0349	+0,06

		ic Rubber						

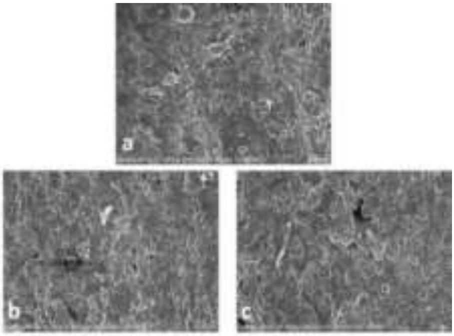

Figure 3.9. SEM image of surface morphology of seal sample immersed in: a) initial sample, b) none additive DO sample and c) additive-blended DO sample

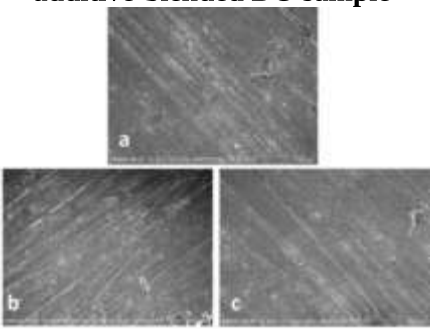

Figure 3.10. SEM image of surface morphology of a high-pressure pump piston sample immersed in: a) initial sample, b) none additive DO sample and c) additive-blended DO sample

At the same time, both fuels have no significant impact on the vehicle's fuel-contact components. These results allow to confirm that the new generation nanoemulsion additives, when mixed into the fuel, will not cause any effect on the fuel.

3.5. Additives efficacy testing on bench test

The results of evaluation of the efficiency of the new generation nanoemulsion additives phase fuel compared with the control fuel on the test platform show that using additive blended fuel saves 5.1% of fuel at full load. CO emission reduction is

10.76%, HC is 11.46%, NOx is 11.19% and PM is 5.52% according to ECER 49 cycle (Figure 3.11 and Figure 3.12).

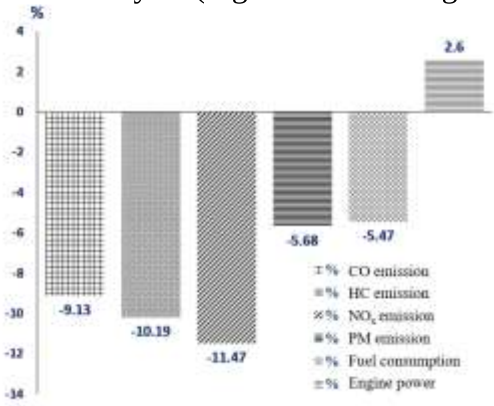

Figure 3.11. The change in power, fuel consumption and emissions of the engine when using additive-mixed diesel compared with conventional diesel according to the speed curve

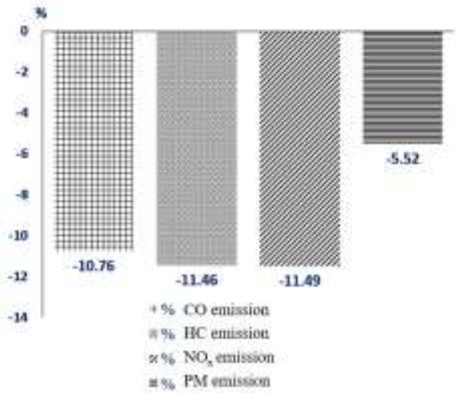

Figure 3.12. Change in CO, HC, NOx and PM emissions of additive phase DO compared to DO-0.05S according to ECER49 cycle

3.6. Field test

For mine trucks using diesel engines: Using new generation additives blended fuel helps to save an average of 5% (Figure 3.13). CO emissions decreased by an average of 6.08%. NOx emissions decreased by about 24% - 25% (figure 3.14). After using the additive, the engine still worked well and stably.

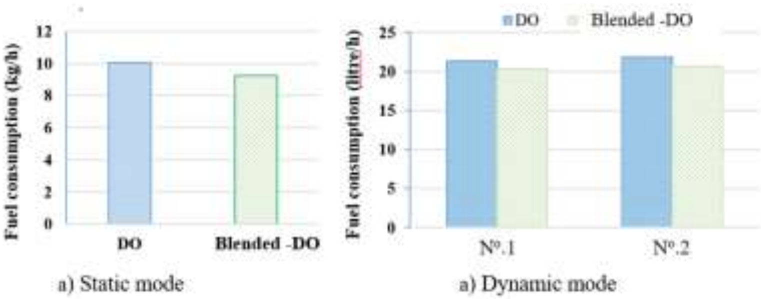

Figure 3.13. Test results for measuring fuel consumption

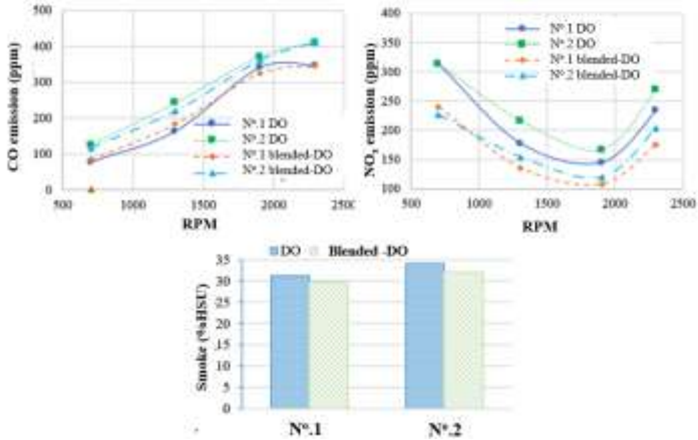

Figure 3.14. Test results of emission measurement on mine trucks

CONCLUSION

1. The surfactant compounds for making new generation nanoemulsions had been successfully synthesized, including:

+ The synthesis of ethoxylated coconut oil diethanolamide, from coconut oil methyl ester, diethanolamine and ethylene oxide, includes two stages, the conversion of coconut oil methyl ester and diethanolamine to coconut oil diethanolamide and the ethoxylation of diethanolamide coconut oil to diethanolamide ethoxylated coconut oil with optimal conditions: molar ratio amine:ester=1.6, temperature 154^{o}C , time 6 hours. Under these conditions, a product yield of over 91% is obtained. The content of ethoxylated coconut oil diethanolamide in the product reaches over 99%. The obtained ethoxylation products contain ethylene oxide groups from 1 to 16 (concentrated in the range of 8). The HLB value range of the product is 6 - 8.

+ Synthesis of fatty acid hydroxyethyl imidazoline fatty acid from tall oil from N-(2-Hydroxyethyl)ethylenediamine and fatty acids from tall oil with optimal conditions: Molar ratio of amine:acid = 1.8, temperature of stage 1 is 140^oC for 6 hours and stage 2 is 250^oC, 5 mmHg for 2 hours. Under these conditions, a yellow-brown product with the properties of the hydroxyethyl imidazoline compound was obtained, with an yield of over 92%.

+ Synthesis of fatty acid polyethylene glycol ester by trans-esterification reaction between methyl oleate and polyethylene glycol using MgO catalyst and heat-treated hydrotalcite catalyst at the following conditions: Molar ratio of methyl oleate:PEG = 2/3 , pressure drop at 0.1 atm, catalyst content 5% of raw material weight, reaction temperature 180^oC for 100 minutes. This surfactant has the ability to stabilize the nanoemulsion system in the reverse nanoemulsion additive when combined with the 2 surfactants prepared above.

2. The preparation of the new generation nanoemulsion additives including water-in-oil nanoemulsions dispersed at the nanoscale using a mixture of 3 surfactants (ethoxylated coconut oil diethanolamide, hydroxyethyl imidazoline and polyethylene glycol ester) and high-power ultrasonic dispersion method and nano iron oxide emulsion additive composition, had been studied. Additive for fuel efficiency on the test platform is 5.1% at full load and CO emissions reduction is 10.76%, HC reaches 11.46%, NOx reaches 11.19% and PM reaches 5,52%, according to the ECER 49 cycle at a low mixing ratio of 1/8,000 by volume with a fuel nanoemulsion particle size of 2-4 nm, without affecting the basic properties of the fuel according to TCVN 5689:2018 and parts in direct contact with the fuel of the engine.

3. The application of nanoemulsion additives had been tested on mining trucks and obtained good results in fuel

consumption and emission reduction, consistent with the research results on the bench test.

4. The mechanism of activation of the new generation nanoemulsion additives had been proposed based on the combination of micro-explosion phenomenom and heterogeneous nanocatalysts has been proposed in enhancing the combustion efficiency of diesel fuel and reducing toxic gas emissions and soot.

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- **C- LIST OF SCIENTIFIC REPORTS**
- **Scientific reports**

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- **Conference**

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