MINISTRY OF EDUCATION AND TRAINING
THE UNIVERSITY OF DANANG

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RESEARCH ENHANCEMENT ON OCTAN NUMBER OF GASOLINE BY ADDING ADDITIVES UNLEADED AND COMMERCIAL APPLICATION

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A. DISSERTATION INTRODUCTION

1. Significances of dissertation

Energy plays an important role in the socio-economic development and improvement of life quality in the nations worldwide, thus the sustainable socio-economic development policy in each country are tight cohesion between national security, economic security and energy security.

Energy has become an inseparable factor from human life, therefore,human being has to face with an alarming situation when traditional energy sources are being exhausted due to indiscriminate exploitation and utilization. The developed nationsimplement super project to exploit fuel from underground, and its large plants continually release tons of toxic gases into the environment which causesglobalwarming.

Among petroleum products, gasoline is an essential commodities whichhas a great influence on people’s lives. The improvement ofgasoline quality primarily is to raiseits octane numberwhich has been conducting a long time so thateconomic value and utilization value of petrol will increase. We have chosen dissertation topic: ***"Advanced research on octane numberof gasoline withunleaded additives and commercial application form"*.**

2. Subjects and tasks of the dessertation

- To find preparation and optimal ratio between additives (ethanol, butanol, MMT, Ferrocene, CN120, Antiknock 819) and gasolines(naphtha, RON 83, RON 90, RON 92) to improve octane number.
- To provide blending process upon ethanol, butanol, MMT, Ferrocene, CN120 and Antiknock 819, determine the additive rate mixinginto gasoline and ensure that gasoline after blending are consistent with Vietnam Standards.
- Based on obtained results to propose applications in manufacturing real products in order to achieve economic and environmental efficiencies and

to set basis for the process of commercial preparation in oil and gas processing facilities.

- To contribute to the national development and roadmap for biofuel use by the Government.

3. New findings of the dissertation

- Has created various biogasolines in accordance with regulated quality of the State.
- Have demonstrated that ethanol of domestic production matched with quality standards for making biogasolines under quality standards.
- In the first research in Vietnam, we have studied the use of CN120 additive ofdomestic production in combination with ethanol of domestic production mixwith gasolines to enhance octane number and gasoline targets which is evaluated in accordance with TCVN.
- Has developed some technological processes on mixing biogasoline with the combination of additives to produce petroleum products with better quality and ensure economic and environmental aspects.

B. CONTENT OF DESSERTAION

Chapter 1. Overview

1. Gasoline

Has generalized documents on gasoline, its chemical compositions and its important physical and chemical indicators.

- Gasoline plays an important economic role in social life. It is crucial to the economic development of each country.
- Demand for gasoline is increasing in line with the social development.
- The more fuels are used, the more polluted environment is.Emissions from motor vehicles are major and dangerous sources causing atmosphere polution.
- The traditional energy sources are increasingly exhausted. The major cause is indiscriminate exploitation and utilization. Therefore, there is a

need for additional sources of additives to increase utilization effciency and reduce environmental pollution.

2. Additives

Has synthesized materials on all kinds of additives (ethanol, buthanol, MMT, Ferrocene, Antiknock 819, CN120)

- In the worldwide, the use of additives (ethanol, MMT, Ferrocene, Antiknock 819 has been researched tomixinto gasoline, which aims to replace previous toxic additives, focuseson improving gasoline quality, minimizes environmental impacts while looking for an alternative fuel source for fossil fuels.
- Utilization efficiency of additives is the improvement of octane number in gasoline with low octane number.
- CN120 additive is produced domestically which is in completed experiment for gasoline preparation to ensure requirements on the gasoline quality under the new standards, in accordance with provisions of quality in the world, consistent with Euro 3, Euro 4, Euro 5 standards and to minimize factors affecting the environment. Mixing CN120, ethanol additiveswith gasoline produced domestically to improve the quality of gasoline.
- The use of additives for mixing with gasoline is to enhance octane number, improve environmental targets, achieve objects under the route using biofuels and additives of the Government, conformity with norms of Vietnamand many other countries.

Chapter 2. Content and research methods

2.1. Raw materials and additives

2.1.1.Additives

- Ethanol 99,5%.
- Buthanol 99,8% .
- MMT additive
- Ferrocene additive
- CN120 additive

- Antiknock 819 additive

2.1.2.Types of gasoline

- Naphtha has low octan number of 70
- RON 83 has octan number of 83 or more
- RON 90 has octan number of 90 or more
- RON 92 has octan number of 92 or more

2.2. Research methods

- Method of analyzing octane number ASTM D 2699
- Method of analyzing lead content ASTM D 5059
- Method of analysis distilled fractionation ASTM D 86
- Method of analyzing corrosion of pieces of copper ASTM D 130
- Methods of analyzing realistic plastic content STM D 381
- Methods of analysis oxidative stability ASTM D 525
- Method of analyzing sulfur content ASTM D 5453
- Method of analyzing vapor pressure (Reid) ASTM D 5191
- Method of analyzing benzene content ASTM D 5580A
- Method of analyzing aromatic hydrocarbons ASTM D 1319
- Method of analyzing olefin ASTM D 1319
- Method of analyzing oxygen content ASTM D 4815
- Method of analyzing net weight ASTM D 4052
- Method of analyzing metal content (Mn, Fe) ASTM D 3831

Chapter 3 Results and Discussion

3.1. Selection of gasoline model

3.2. Quality assessment of additives (ethanol, buthanol, MMT, ferrocene, Antiknock 819, CN120)

To test the quality of additives mixing into the gasoline, we analyze nuclear magnetic resonance spectroscopy of additive models such as ethanol, buthanol, MMT, ferrocene, Antiknock 819, and chromatography - mass spectrometry.

3.2.1. Ethanol

GC-MS analysis

We analyzed ethanol samples to determine its purity by GC-MS. Chromatogram obtained in Figure 3.1 shows the presence of main peak at the highest intensity in retention time of 1,826 minutes. When we looked up in the spectrum bank, we found that spectrum obtained at this peak is in corresponding to ethanol compounds with content of 99.8 percent of the total volume. This confirms that ethanol has purity of 99.8.

Figure 3.1. Chromatogram of ethanol

3.2.2. Buthanol

GC-MS analysis

We analyzed buthanol samples to determine its purity by GC-MS. Chromatogram obtained in Figure 3.2 shows the presence of main peak at the highest intensity in retention time of 3,703 minutes. When we looked up in the spectrum bank, we found that spectrum obtained at this peak is in corresponding to 1-butanol compounds with content of 99,9 percent of the total volume. This confirms that ethanol has purity of 99,9.

Figure 3.2. Chromatogram of buthanol

3.2.3. MMT

On the ^{1}H-NMR spectrum of MMT appeared signal of the methyl group at δ_H 2,03. In addition, the proton signal of the cyclopentadienyl ring appear in the region from δ_H 6,96 đến 7,29.

^{13}C-NMR spectra also allows identifying the presence of the methyl carbon signal at δ_C 20,33, CH signals in the region from δ_C 125,59 đến 129,91, and quaternary carbon signal at δ_C 137.78. The spectral data obtained demonstrated the presence of additive methylcyclopentadienyl manganese tricarbonyl.

3.2.4. Ferrocene

Bisxiclopentadienyl Ferrocene or iron Fe $Fe(C_5H_5)_2$ is quality orange crystals, t^o_{nc}= 173^{o}C, t^o_s= 249^{o}C. Molecular $Fe(C_5H_5)_2$ type structure have pancakes, with Fe 2 + ions between two parallel planes of two adjacent ion $C_5H_5^-$ year mortality**.**

On the ^{1}H NMR spectrum, 5 H atom equivalent of $C_5H_5^-$ cyclopentadienyl resonance at the same frequency and has shifted chemical shift very much for strong field region (δ = 4.1 ppm) compared with signals Csp^2 normal direction of benzene rings (approximately 7 ppm) and alkenes (about 6 ppm), due to the effect of density blanket high e. Likewise, all 5 C atom resonates at the same frequency and has moved many chemical shifts of strong field region (δ = 70 ppm) than the signal of benzene and alkene Csp^2 casualties (on 100 ppm).

3.2.5. Antiknock 819

On the ^{1}H-NMR spectrum of Antiknock 819 appears proton signals of an aromatic ring that is positioned at δ_H 6,55 (d, J = 8,0 Hz), 6,67 (t, J = 8,0 Hz), and 7,18 (t, J = 8,0 Hz). A methyl group attached to the nitrogen atom is determined at δ_H 2,80 (s).

^{13}C-NMR spectra of Antiknock 819 also signals appear characteristic of an aromatic ring at a position that was δ_C 112,49 (CH × 2), 117,26 (CH), 128,95 (CH × 2) and 148.84 (C). In addition, the methyl carbon signals were determined at 30.10 (CH_3). The spectral data indicated showed the presence of N-methylaniline and aniline.

3.2.6. CN120

^{1}H-NMR spectra of CN120 appearance signals a methyl group at δ_H 2,76 (s) and the aromatic proton signals in the case of δ_H from 6,56 to 7,18. In the high schools in the ^{13}C-NMR spectrum of the CN120 only appear at δ_C methyl signal 30.56. In the low case, the signal of the aromatic ring methyl appearing at 112.31 to 129.16 δ_C and quaternary carbon signals of the aromatic ring at δ_C 149.27. The spectral data showed the presence of N-methylaniline compound.

*** Comments:**

The additives which is used in mixing gasolines such as ethanol, butanol have high purity assuring requirements for mixing with gasoline. For additives like MMT and ferrocene, major components are methylcyclopentadienyl manganese tricarbonyl compounds and iron cyclopentadienyl compounds which raise octance number after mixing into gasoline. CN120 and 819 Antiknock additives with main components of N-methylaniline and Aniline are the substance with high octane number helping to raise gasoline octane after mixing.

3.3. Quality criteria of gasoline mixing ethanol

3.3.1. The process of preparation

We conducted sampling RON 90, samples of C1, C2, C3, C4, C5 are mixed with ethanol in different ratios of volume from 1 percent to 10 percent by volume of ethanol in gasoline. The gasoline samples are mixed with ethanol in volume flask of 1 liter, then those samples were transferred into glass bottles with abrasive button, shaked and mixed well. Next, they were kept in refrigerator at the specified temperature (from 0÷4^{o}C) to determine the physical and chemical indicators of gasoline.

Then samples were analyzed someaffected indicators of gasoline quality when mixed ethanol according to Vietnam Standards 6776: 2005 including oxygen content, octane number, saturation vapor pressure, sulfur content, distillation composition, net weight.

3.3.2. Oxygen content

Result of analysing criteria of oxygen content of gasoline sample C1, C2, C3, C4 and C5 before and after mixing etanol presented in Image 3.8

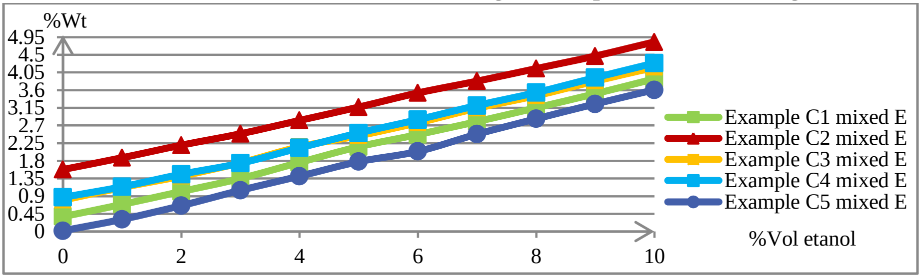

Image 3.10. Graph shows the dependence of oxygen content of gasoline samples C1, C2, C3, C4 and C5 on vol% ethanol

***Comment:**

Result in image 3.10 shows that if etanol content is in gasoline, oxygen content increases. It can be explained as the more amount of ethanol is mixed, the more total oxygen content increases.

3.3.3. Octan numeric value

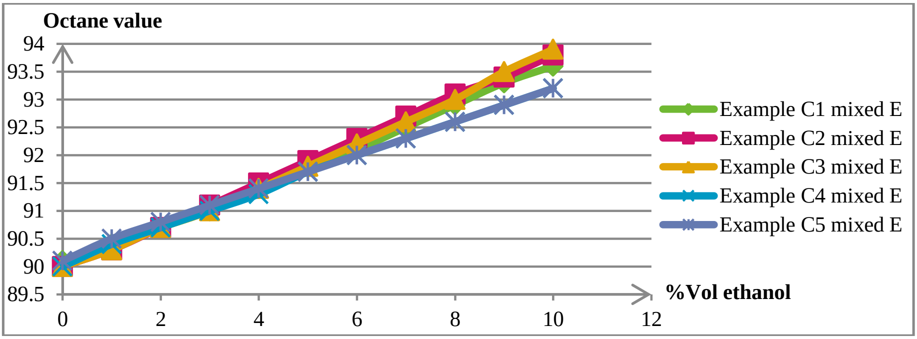

Image 3.11. Graph shows the dependence of octan numeric value of gasoline samples from C1, C2, C3, C4, C5 mixed ethanol on % ethanol volume

***Comment:**

- Result in image 3.11 shows the dependence of octan numeric value of gasoline samples on ethanol volume mixed.
- Ethanol gasoline increases octan numeric value compared with initial original gasoline sample. Octan numeric value of gasoline samples increase steadily in accordance with mixed ratio.
- At mixed ratio 6% of ethanol volume, octan numeric value of gasoline samples reaches standard of gasoline RON 92 in accordance with TCVN 6776:2005.

3.2.4. Saturated vapour pressure

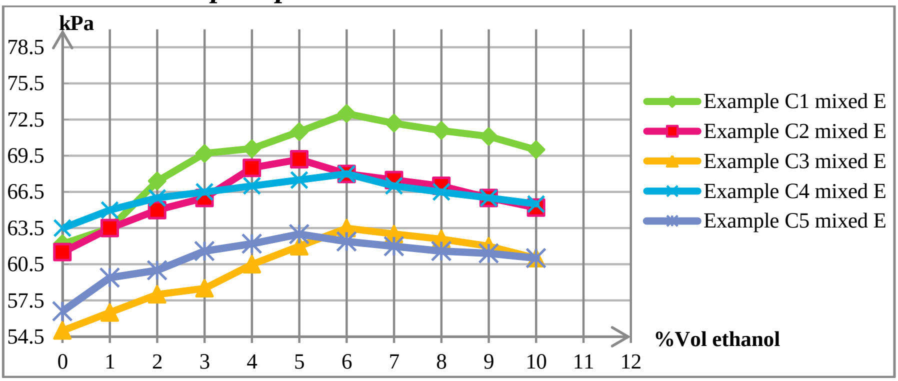

Image 3.12. Graph shows the dependence of saturated vapour pressure of gasoline examples from C1, C2, C3, C4, C5 mixed ethanol on % ethanol volume

***Comment:**

Through data result in image 3.12, we can see that mixing ethanol into gasoline will increase saturated vapour pressure of mixture, this pressure increases to a maximum point, then decrease in accordance with etanol content in gasoline.

Conclusion 1

- *For original gasoline samples, depending on oxygen content in original gasoline sample, can mix corresponding ethanol content to gasoline sample; for original gasoline samples with oxygen content less than 0,9%*

of volume, can mix 5% volume of ethanol into gasoline. Oxygen content analysis TCVN consistent.

- *The gasoline sample with oxygen content less than 0,2% of volume, criteria of octan numeric value ≥ 90,0, can mix maximum 7% volume ethanol of oxygen content and octan numeric value reaches standard of gasoline RON 92 in accordance with TCVN 6776:2005.*
- *Mixing 5% volume etanol into gasoline with octan numeric value increasing about 1,5 to 1,8 unit.*
- *Ethanol also changes the saturated vapour pressure of the mixture, the change here is not linear; it follows a curve and has maximum point.*
- *All the following gasoline samples, after mixing ethanol, the remaining analysis criteria are consistent with TCVN 6776:2005, except for octan numeric value criteria and oxygen.*

3.4. Analysis result of gasoline RON 92 before and after mixing MMT, ferrocene, ethanol

3.4.1. Mixing MMT

Conclusion 2

- *MMT with rate of 19 mg/l, Mn content increases not exceed 5 mg/l and octan numeric value increase from 0,9 to 1,0 octan unit.*
- *Gasoline RON 92 with initial octan numeric value= 92.0 after mixing 19 mg/l of MMT and 7% of ethanol volume, octan numeric increases to 95,0 reaching technical criteria of gasoline RON 95 in accordance with TCVN 6776:2005*
- *Gasoline RON 90 with octan numeric value = 90.1 after mixing 19 mg/l MMT additive and 3% of ethanol volume 92 octan in accordance with the technical standards of 92 RON gasoline according to TCVN 6776:2005.*
- *Results of the analysis criteria and test fits with TCVN 6776:2005. Some criteria related to environment as sulphur, benzene, aromatic hydrocarbon, olefin content decrease compared with original gasoline sample when haven't mixed yet.*

3.4.2. Mixing ferrocene

Conclusion 3

- *Mixing ferrocene with the rate of 16 mg/l, Fe content increases not exceed 5 mg/l, in accordance with TCVN 6776:2005, and octan numeric value increase from 0,9 to 1,0 octan unit.*
- *Gasoline RON 92 with octan numeric value = 92,3 after mixing 16 mg/l ferrocene and 5% volume ethanol, octan numeric value increases to 95,0, reaching technical criteria of gasoline RON 95 in accordance with TCVN 6776:2005.*
- *Gasoline RON 90 with octan numeric value = 90,0 after mixing 16 mg/l ferrocene and 3% volume ethanol numeric value, reaching 92,0 in accordance with the technical criteria of gasoline RON 92 in accordance with TCVN 6776:2005.*
- *The gasoline sample after mixing ferrocene and etanol, some criteria related to environment as sulphur, benzene, aromatic hydrocarbon, olefin content decrease compared with original gasoline sample when haven't mixed yet.*
- *The remaining criteria is in accordance with TCVN 6776:2005; analysis in accordance with TCVN.*

3.5. Analysis result of gasoline sample RON 90 BEFORE, after mixing MMT, ferrocene and buthanol

Conclusion 4

- *When mixing 11% volume of buthanol and 19 mg MMT into 1 litter of gasoline RON 90, octan numeric value increases to 92.1, reaching criteria of octan numeric value of gasoline RON 92; the analysis functions reaching TCVN 6776:2005.*
- *Results of simultaneous mixing 11% buthanol volume and 16 mg of ferrocene into 1 litter of gasoline RON 90, octan numeric value increases from 90,0 to 92,1, reaching criteria of gasoline RON 92 according to TCVN 6776:2005; the analysis functions reaching TCVN 6776:2005.*

3.6. Analysis result of gasoline before and after mixing CN120, Antiknock 819 and ethanol

3.6.1. Original gasoline samples before mixing

- Sample A1: Naphtha gasoline - Sample B1: Gasoline RON 83
- Sample C11: Gasoline RON 90 - Sample D4: Gasoline RON 92

3.6.2. Result of analyzing gasoline samples as Naphtha, RON 83, RON 90, and RON 92 mixed

Selecting gasoline samples as Naphtha, RON 83, RON 90, and RON 92 in A1, B1, C11, and D4 at mixed ratio with ethanol is 7% volume (at this ratio, oxygen content reaches quality in accordance with TCVN 6776:2005); then, implementing to analysis all quality criteria of gasoline samples at the rate of 7% volume of ethanol in accordance with TCVN 6776:2005.

3.6.3. Result of analyzing gasoline samples as Naphtha, RON 83, RON 90, and RON 92 mixed etanol and CN120

Selecting gasoline samples as A1, B1, C11, D4 mixed 7% volume of ethanol; then, take these samples to mix with CN120 in accordance with volume ratio from 0,5%, 1%, 1,5%, 2%, 2,5%, 3%, 3,5%, 4%, 4,5% and 5%; implement to analysis and assess some criteria affected to gasoline quality after mixing.

3.6.3.1. Octan numeric value

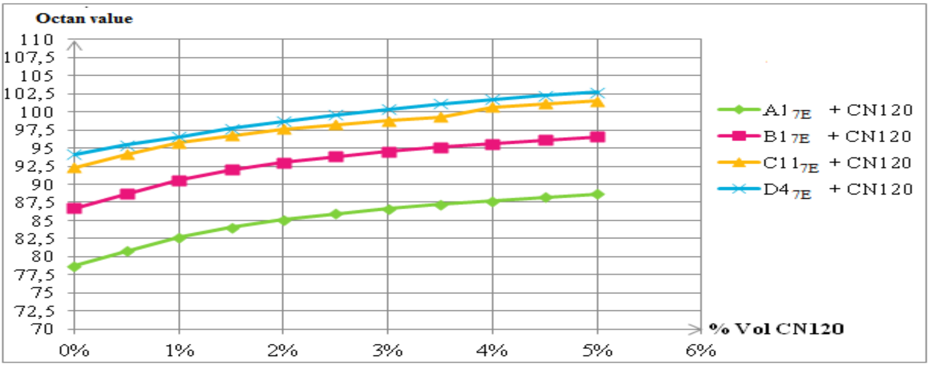

Image 3.21. Graph shows the dependence of octan numeric value, sample $A1_{7E}$, $B1_{7E}$, $C11_{7E}$, $D4_{7E}$ on ethanol volume and CN120

*** Comment:** result in image 3.21 shows that gasoline sample A1, B1, C11, D4 after mixing 7% volume of ethanol and CN120, octan numeric value of gasoline samples increases when volume of CN120 in the sample increases.

- Sample $A1_{7E}$ at the rate of 5% volume of CN120, octan numeric value increases 10 octan units, with mixing ratio is 5% of CN120, oxygen content suits with TCVN but octan numeric value = 88,7 does not reach TCVN of gasoline RON 92.
- Sample $B1_{7E}$ at the mixing ratio of 1,5% volume of CN120, octan numeric value increases by 5,3 octan units to 92,0, reaching the standards of gasoline RON 92 according to TCVN 6776:2005.
- Sample $C11_{7E}$ at the mixing ratio of 1,0% volume of CN120, octan numeric value increases by 3,4 octan units to 95,7, reaching the standards of gasoline RON 95 according to TCVN 6776:2005.
- Sample $D4_{7E}$ at the mixing ratio of 0,5% volume of CN120, octan numeric value increases by 1,3 octan units to 95,4, reaching the standards of gasoline RON 95 according to TCVN 6776:2005.

3.6.3.2. Gum content

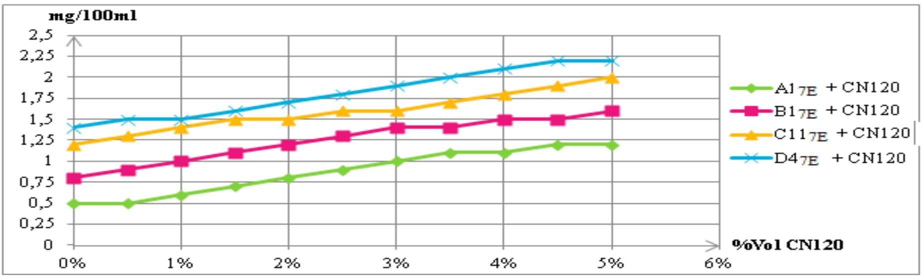

Image 3.22. Graph shows the dependence of gum content of gasoline samples $A1_{7E}$, $B1_{7E}$, $C11_{7E}$, $D4_{7E}$ on the volume of ethanol and additive CN120

*** Comment:**_With the result of image 3.22, it is noticed that the gasoline samples A1, B1, C11, D4 after being mixed with 7% volume of ethanol and additive CN120, gum content has changed together with added volume of additive CN120, gum content increases but very little, and is in accordance with TCVN 6776:2005.

3.6.3.3. Aromatic hydrocarbon content

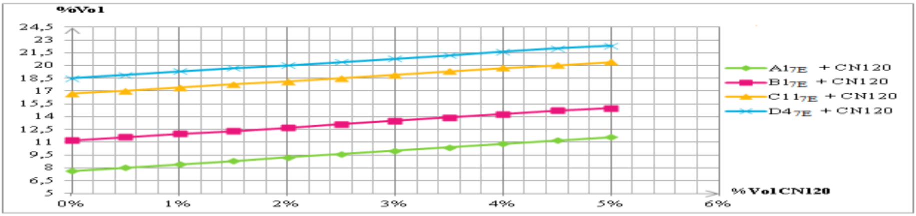

Image 3.23. Graph shows the dependence of aromatic hydrocarbons content value of gasoline samples A1$_{7E}$, B1$_{7E}$, C11$_{7E}$, D4$_{7E}$ on the volume of ethanol and CN120

*** Comment:** With the result of Image 3.23, it is noticed that after being mixed with 7% volume of ethanol and additive CN120, aromatic hydrocarbon content has increased together with the added volume of CN120 but it is still in accordance with TCVN 6776:2005.

Conclusion 5

- *When adding additive CN120 to samples of gasoline with lower octan numeric value, octan numeric value increases higher than samples with high octan numeric value.*
- *Gasoline sample naphtha mixed with 7% volume of ethanol and 5% volume of additivi CN120 still does not reach standards of gasoline RON92.*
- *Gasoline RON 83 mixed with 7% volume of ethanol and 1,5% volume of additivi CN120, octan numeric value reaches 92,0; mixed with 7% volume of ethanol and 3,5% volume of additivi CN120, octan numeric value reaches 95,1.*
- *Gasoline RON 90 mixed with 7% volume of ethanol and 1% volume of additivi CN120, octan numeric value reaches 95,7.*
- *Gasoline RON 92 mixed with 7% volume of ethanol and 0,5% volume of additivi CN120, octan numeric value reaches 95,4.*
- *Results of the analysis of the sample gasoline criteria after being mixed with ethanol and additive CN120, it is in accordance with TCVN 6776:2005.*

3.6.4. The results of analyzing gasoline samples Naphtha, RON 83, RON 90, RON 92 mixed with ethanol and additive Antiknock 819

Choose the gasoline samples naphtha, RON 83, RON 90, RON 92 mixed 7% volume of ethanol, then mixing the samples with additive Antiknock 819 according to the volume ratio 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5%, 5%. Conduct analysis and assessment of some targets affecting the quality of gasoline after being mixed.

3.6.4.1. Octan numeric value

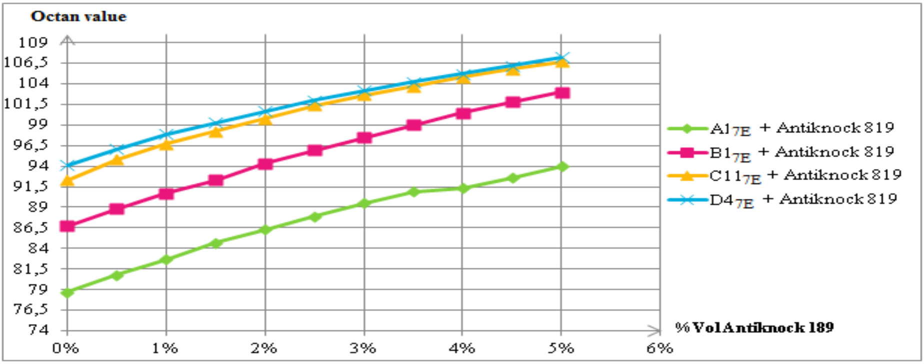

Image 3.26. Graph shows the dependence of octan numeric value of gasoline samples $A1_{7E}$, $B1_{7E}$, $C11_{7E}$, $D4_{7E}$ on the volume of ethanol and Antiknock 819

*** Comment:**

- With the result of image 3.26 it is noticed that gasoline samples A1, B1, C11, D4 after being mixed with 7% volume of ethanol and additive Antiknock 819, there are changes as follows:
- Gasoline sample $A1_{7E}$, at the mixing ratio of 4,5% volume of Antiknock 819, octan numeric value = 92,6 in accordance with gasoline RON 92 under TCVN 6776:2005.
- Gasoline sample $B1_{7E}$, at the mixing ratio of 1,5% volume of Antiknock 819, octan numeric value = 92,3 in accordance with gasoline RON 92 under TCVN 6776:2005; at the mixing ratio of 2,5% volume of Antiknock 819, octan numeric value = 95,9 in accordance with gasoline RON 95 under TCVN 6776:2005.

- Gasoline sample C11$_{7E}$, at the mixing ratio of 1,0% volume of Antiknock 819, octan numeric value = 96,7 in accordance with gasoline RON 95 under TCVN 6776:2005.
- Gasoline sample D4$_{7E}$, at the mixing ratio of 0,5% volume of Antiknock 819, octan numeric value = 96,1 in accordance with gasoline RON 95 under TCVN 6776:2005.

3.6.4.2. Aromatic hydrocarbon content

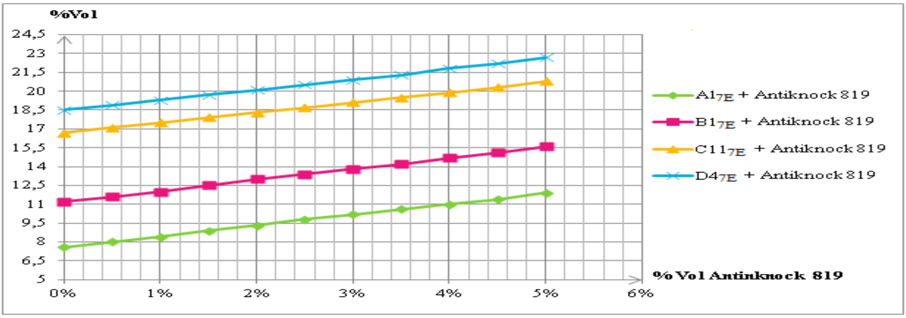

Image 3.27. Graph shows the dependence of aromatic hydrocarbon content of gasoline samples A1$_{7E}$, B1$_{7E}$, C11$_{7E}$, D4$_{7E}$ on the volume of ethanol and Antiknock 819

* Comment: With the result of Image 3.27 it is noticed that samples A1, B1, C11, D4 after being mixed with 7% volume of ethanol and additive Antiknock 819 aromatic hydrocarbons content changes and conforms to TCVN 6776:2005.

3.6.4.3. Gum content

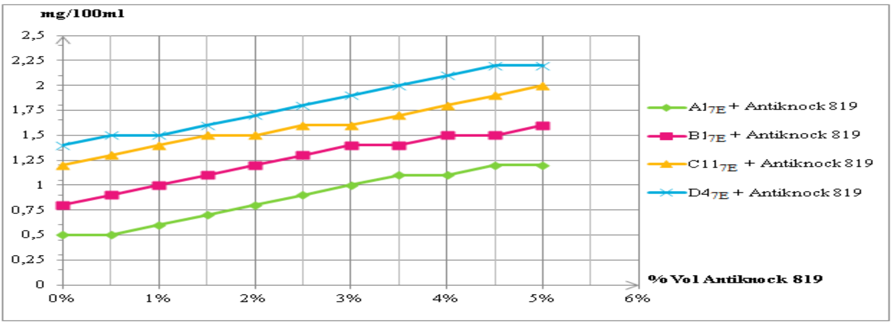

Image 3.28. Dependence graph of gum content of gasoline samples A1$_{7E}$, B1$_{7E}$, C11$_{7E}$, D4$_{7E}$ on the volume of ethanol and additive Antiknock 819

*** Comment:** With the result of Image 3.28 it is noticed that samples A1, B1, C11, D4 after being mixed with 7% volume of ethanol and additive Antiknock 819, gum content increases but very little and conforms to TCVN 6776:2005.

Conclusion 6

- *All gasoline samples naphtha, RON 83, RON 90, RON 92 after being mixed with 7% volume of ethanol and 5% volume of additive Antiknock 819, samples after being mixed and analyzed are in accordance with TCVN 6776:2005 and QCVN 1:2009/BKHCN.*
- *Additive Antiknock 819 mixes with gasoline with the same target volume unit, octan numeric value increases higher than additive CN120.*
- *For gasoline RON 90, after being mixed with 7% volume of ethanol and additive Antiknock 819 can be mixed with the less rate of under 1% to reach the standards of gasoline RON 95.*
- *Additive Antiknock-819 is an organic additive, so when being mixed, aromatic hydrocarbons content increases, but still consistent withwith regulations of TCVN.*

3.7. Assessing exhaust gasoline content mixed with buthanol, MMT, ferrocene, CN120, Antiknock 819 ethanol–blended gasoline

3.6.1. Result on measurement of content of CO_2, CO, NO_x, HC as exhaust gases in gasoline: Naphtha, RON 83, RON 90, RON 92 blended with ethanol, butanol, MMT, ferrocene, CN120, Antiknock 819

Table 3.37: Result on measurement of exhaust gas component

TT	Exhaust / Sample		CO_2 (ppm)	CO (ppm)	NO_x (ppm)	HC (ppm)
1	C1	**C1 (original sample)**	3,56	0,66	11,2	291
		C1 + 6%Vol etanol	2,73	0,47	8,8	236
2	D1	**D1 (original sample)**	4,59	1,42	17,8	365
		D1 + MMT + 7% Vol etanol	3,12	1,01	14,2	267
	D2	**D2 (original sample)**	5,12	1,78	17,5	390

3		D2 + ferrocene + 7% Vol ethanol	4,05	1,49	15,6	303
4	C8	**C8 (original sample)**	5,95	1,68	19,2	290
		C8 + ferrocene + 7% Vol ethanol	5,74	1,54	14,6	223
5	C9	**C9 (original sample)**	5,84	1,59	23,6	340
		C9+ MMT + 11% Vol buthanol	5,70	1,40	18,4	286
6	B1	**B1 (original sample)**	3,32	5,64	18,1	418
		B1 + 7% Vol ethanol +1,5% Vol CN120	3,03	5,21	25,4	321
		B1 + 7% Vol ethanol + 1,5% Vol Antiknock 819	3,11	5,19	25,0	330
7	D4	**D4 (original sample)**	5,25	4,78	20,0	492
		D4 + 7% Vol ethanol +1,5% Vol CN120	4,97	4,30	26,9	400
		D4 + 7% Vol ethanol + 1,5% Vol Antiknock 819	5,05	4,19	26,2	403

*** Comments:**

- For ethanol-blended gasoline, combustion process will reduce content of exhaust gases such as CO, CO_2, HC, NO_2
- Content of exhaust gas such as CO, CO_2, HC, NO_2 in Gasoline blended with MMT or ferrocene is the same as those in ethanol-blended gasoline.
- Content of exhaust gas such as CO, CO_2, HC, NO_2 in Gasoline blended with butanol and MMT or ferrocene is the same as those in ethanol-blended gasoline.
- Gasoline blended with ethanol and CN120, Antiknock 819, temperature in combustion chamber will increase content of NO_x , but the content of NO_x is increased due to not only nitrogen in addtitive but also the oxidation of nitrogen in the air.

Conclusion 7

1. *Criteria of analysis of CO, HC are in compliance with emission standards TCVN 6438:2001 - Means of road traffic - the maximum allowable limit of exhaust gas.*
2. *Using gasoline blended with ethanol and additives mainly are to minimize content of exhaust gas, but some gases are increased insignificant according to regulations in TCVN. Concerning total decreased exhaust gases, it is better to use gasoline blended with additives for positive environmental impact.*
3. *Concerning environment: Ethanol-blended gasoline increases capacity to burn out fuel; therefore, content of exhaust gas into environment is significantly decreased through reduction of content of sulphur, benzene, aromatic hydrocarbons, the result is that content of exhaust gas into environment is reduced.*

3.8. Results of quality assessment of gasoline mixid with additives during preservation and storage

To assess the quality of the gasoline after mixing additives within 1 month of preservation. We sampled those mixed gasoline according to the optimum ratio was analyzed in section 3.2 and 3.5. The samples after preparation are analyzed the quality. Criteria were evaluated according to Vietnam Standards 6776: 2005. At the same time, we stored those sample in 1 month and analyzed all of the gasoline quality standards in line with Vietnam Standards 6776: 2005. The prepared samples conducted additives to perform quality assessment include:

- RON 90 mixed 6% of ethanol volume
- RON 92 mixed MMT and 7% of ethanol volume
- RON 92 mixed Ferrocene and 7% of ethanol volume
- RON 90 mixed MMT and 11% of butanol volume
- RON 83 mixed 7% of ethanol volume and 1.5% of CN120 volume
- RON 83 mixed 7% of ethanol volume and 1.5% of Antiknock 819 volume

Conclusion 8

The analytical results of the quality assessment of RON 83, RON 90, RON 92 mixed ethanol, butanol, MMT additive, Ferrocene, CN120, 819 Antiknock immediately after preparation and after 1 month storage show that all chemical and physical indicators of those samples does not change much compared. All targets are analyzed in accordance with Vietnam Standard 6776: 2005 for unleaded gasoline RON 92 and RON 95. Thus, mixing additives to increase octane number does not affect the nature of the fuel in the the storage and preservation within a month.

3.9. Results of assessingcompatibility of gasoline mixed additives affecting materials

We took gasket (buffer) of the Ford car in gasoline container, soaked in the original gasoline samples and mixedgasoline samples. Then we measured on stereoscopic microscope at the Center for Analysis and Classification, Danang Branch-General Department of Customs, specifically:

- RON 90 mixes with 7% of ethanol volume
- RON 92 mixes with MMT and 7% of ethanol volume
- RON 92 mixes with MMT and 7% of ethanol volume
- RON 90 mixes with MMT and 11% of ethanol volume
- RON 83 mixes with 7% of ethanol volume and 1.5% CN120 volume, RON 83 mixes with 7% of ethanol volume and 1.5% of Antiknock 819 volume

Conclusion 9

- The result of measurement of rubber gasket (buffer) samples of Ford cars on stereoscopic microscope shows that the surface of sample soaked in gasoline, gasoline mixed with ethanol, gasoline mixed with butanol and types of additives such as MMT Ferrocene, CN120, Antiknock 819 (containing aromatic amin addition) almostly don’t change compared to the surface of original sample and the sample soaked in control fuel.
- Therefore, the result of measurement on stereoscopic microscope can conclude that gasoline mixed with additives containing organometallic

compounds; aromatic amine additives do not affect materials such as rubber gasket (buffer). They are fully compatible with this material.

Chapter 4. The research and deployment of technology process of gasoline preparation

From the results obtained in section 3, in order to deploy practical applications of gasoline after preparation, we build the production process to mix gasoline with additives into finished products, on the basis of test investment development of mixing system and export E5 for xitec cars (road gasoline transportation) under the Government route.

4.1. The plan for implementing gasoline preparation production technology

4.1.1. E5 production deployment

Select mixing mothods on pipelines to Tank Cars Station.

Kerosolene (petroleum spirit) and ethanol fuel is pumped simultaneously with defined capacity controlled by valve system associated with the disconnected control box installed on the flowmeter.

The advantage of this method of mixing can be installed at Existing Petrol Filling Station, simple operation, and low investment costs. Because there are more advantages than in mixing method at tank, mixing mothodon the pipe combined with fuel import from the bottom has been widely applied in Thailand biofuel petrol disbursement zone.

4.1.2. Deploying gasoline mixing with ethanol and Antiknock 819, CN120,MMT additives

Select preparation technology and equipment: preparation at the tank, after defining the volume rate of clear gasoline, additives and ethanol, all will be pumped into preaparation tanks. Pumping each part of each additive and gasoline in preparation tanks andpump in preparation process. After pumping enough additives and gasoline, used stirrer to stir and mix... After blended, the quality of finished gasoline will be checked. If finished gasoline is enough quality, they wiil sold to ships, barges and xitec truck as conventional gasoline.

4.1.3. Mixing gasoline with ethanol and Ferrocene additive

Selection preparation technology

Because Ferrocene additives are powdered, so before mixing ferrocene additive with defined ratio, mix with gasoline to change to liquid condition, then mixing with gasoline and ethanol. Thus, using the mixing system and stirring and mixing Ferrocene additive

Before conducting mixture of petrol, ethanol and ferrocene additive, put Ferrocene additives in the container, so that the pump can operate efficiently and additive ferrocene easily disperse, the gas must be diluted to dissolved Ferrocene additive. In order to mix additives homogeneously, when pumping gasoline, ethanol and Ferrocene additive, pumps dissolved additives with gasoline each 15 minute and mixing with etanol and gasoline until finish mixing.

4.2. Caculate the price finised products after preparation

We rely on E5 production projects to caculate the finised products price after preparation

The annual turnover of the project only refers to interest due to falling gasoline price and calculated as follows:

- Preparation capacity: 100,000 m3 E5 gas / 01 year (95,000 RON 92 gasolines + 5,000 m^3 ethanol)
- Cost of materials (RON 92 gasoline): 24, 210 vnd / 01 liter
- Additives (ethanol): 16,000 VND / 01 liter
- Cost of sold finished products - E5 gasoline (mixed with 5% ethanol): 24,210vnd / 01 liter

On that basis calculate the price per liter of 5% ethanol blended gasoline is 23799.5 vnd/liter.

We also calculated the economic indicators of production projects E5 and the results show the project feasible and the payback period is one year and two months.

THE MAIN CONCLUSION OF THE THESIS

The study, "Octane number Advanced Research of gasoline by unleaded additives, and apply in commodity products" acquired the scientific results as follows:

1. Having successfully blended kinds of gasoline derived from petroleum with additives containing oxygenated compounds, additives containing aromatic compounds, aromatic amines, additives containing organometallic compounds, corresponding to the different rates, creates biofuel products and analyzes and assesses the quality of the mixing gasoline.

- Gasoline mixed with ethanol: petrol form with oxygen content less than 0.9% and may mix 5% volume ethanol into gasoline. Gasoline samples with oxygen content less than 0.2% and octane number is higher or equal 90.0, could mix 7% of ethanol volume in maximum. The sample gas after mixing with oxygen and octane number Vietnam is appropriate for TCVN 6776: 2005.
- Gasoline mixed with butanol: gasoline mixed with 11 percent butanolvolume, measured oxygen content is suitable with TCVN 6776: 2005, octane number increased by 1 octane unit.
- Gasoline mixed with MMT additive, Ferrocene: gasoline with 0 metal content (Mn,Fe) is mixed with 19mg MMT or 16mg Ferrocene additive in 1 liter of gasoline, analyzed Mn or Fe content less than 5mg/liter consistent with ISO 6776: 2005, octane number increased by 1 unit octane.
- Gas mixed with ethanol, butanol and MMT, Ferrocene additive

  + Petrol with 92.0 Octane number, mix with 7 percent of ethanol volume and 19mg/liter MMT additive, or 16 mg /liter Ferrocene additive, Octane number increased and acquires RON 95 technical standards according to ISO 6776:2005.

  + Petrol with 90.0 Octane nubmer mixed 11 % of butanolvolume and 19mg/liter MMT additive, or 16 mg / liter Ferrocene additive, indicators of analysis such as metal content, oxygen content, measured Octane number is higher than or equal to 92.0 in accordance with TCVN 6776: 2005.
- Mixed CN120 additives with ethanol

+ For the gasoline with 83, 0 octane nubmer mix 7% of etanol volume and 1.5 % CN120 additive volume, 92.0 octane number, mix with 7 percent volume etanol and 3.5 percent CN120 additive volume, octan number reached 95.1.

+ Gasoline with 90.0 Octane numbers, mix with 7 percent ethanol volume and 1 percent CN120 additive volume, Octane number reached 96.1.

+ Gasoline with 92.0 Octane numbers, mix with 7 percent ethanol volume and 0.5 percent CN120 additive volume, and Octane number gains 95.4.

- Mix 819 Antiknock additive with etanol

+ RON 90 mixed with 7 percent of ethanol volume and mixes with 819 Antiknock additives with the rate of less than 1 %, volume gains RON95 petrol standards.

+ Gasoline with 83.0 Octane number, mix with 7 percent ethanol volume and 1.5 percent Antiknock 819 additive volume , octane number reached 92.3, mix with 7 percent volume ethanol and 2.5 percent 819 Atiknock additive volume s, Octane number reached 95.9.

2. Use CN120 additives is the only additive produced indigenously, combined with ethanol to mix with gasoline produced indigenously to bring products with better quality compared to gasoline before mixing additives about quality, value and environment.

3. Researched and proposed the implementation plans of gas preparation technology process, capable of deployment in factories, petroleum processing industry with the technological process:

- The gasoline mixing technological process with ethanol (E5 petrol)
- Gas preparation with ethanol and kinds of additives such as CN120, Antiknock 819, and MMT
- Blending gasoline with ethanol and Ferrocene additive

4. First time using preparation additives in combination with ethanol to create gas products after preparation with better quality, meet the technical requirements for the use of vehicles. Calculated the economic effect of gasoline price mixed with additives, the price of finised goods after mixing lower than the current price of products and environmental factors such as air emission of mixing gasoline is better.

SCIENTIFIC WORKS PUBLISHED

[1] Dao Hung Cuong, Nguyen Dinh Thong (2008), "A Research on the increase of MO90 octane rating by using ethanol additive", *Journal of Science and Technology*, The University of Da Nang, 4(27), p.37-42

[2] Nguyen Dinh Thong, Tran Van Thang, Dao Hung Cuong (2009), "Enhancement on octane number of gasoline MO90, MO92 by adding additives MMT and ethanol", *Journal of Chemistry T.47 (2A)*, p.398-403.

[3] Dao Hung Cuong, Nguyen Dinh Thong, Truong Quoc Hung (2009), "Enhancement on octane number of gasoline MOGAS 92 by adding additives ferrocene and etanol", *Journal of Science and Technology*, The University of Da Nang, 40 (book 1), p.53-59.

[4] Dao Hung Cuong, Nguyen Dinh Thong (2010), "Enhancement on octane number of gasoline MOGAS 92 by adding additives MMT and ethanol", *Journal of Chemistry T.48 (4C)*, p.341-345.

[5] Dao Hung Cuong, Nguyen Dinh Thong (2012), "Enhancement on octane number of gasoline RON 90 by adding additives ferrocene and butanol", *Proceedings scientific conference The University of Da Nang*, 5th, p.387-392. v

[6] Nguyen Dinh Thong, Dao Hung Cuong, Tran Van Thang (2013), "Enhancement on octane number of gasoline RON 90 by adding additives CN120 and ethanol", *Journal of Chemistry and Application*, No 1 (17), p.20-23.

[7] Nguyen Dinh Thong, Dao Hung Cuong, Tran Van Thang (2013), "Enhancement on octane number of gasoline RON 90 by adding additives CN120 and ethanol", *Journal of Science and Technology Technical Universities*, No 92-2013, p.131-135.

[8] Nguyen Thi Thanh Xuan, Nguyen Dinh Thong, Tran Van Hai (2013), "Research some additives blended into unleaded gasoline oxygenate", *Industry and Trade Magazines*, No 13-4/2013, p.24-27.

[9] Nguyen Dinh Thong, Dao Hung Cuong, Tran Van Thang (2013), "Enhancement on octane number of gasoline by adding additives CN120 and ethanol", *Journal of Chemistry T.51 (2AB)*, p.515-519.

[10] Nguyen Dinh Thong, Dao Hung Cuong, Tran Van Thang (2013), "Enhancement on octane number of gasoline by adding additives Antiknock 819 and ethanol", *Journal of Chemistry T.51 (2C)*, p.1003-1007.

[11] Nguyen Thi Thanh Xuan, Nguyen Dinh Thong, Tran Van Hai (2013), "Effects of blending Antiknock 819 with gasoline to improve fuel antiknock 819 properties", *Journal of Science and Technology*, The University of Da Nang, 4 (66), p.106-112.

[12] Nguyen Dinh Thong, Dao Hung Cuong, Tran Van Thang (2013), "Enhancement on octan number of gasoline by adding additives unleaded", *Proceedings scientific conference Vietnam – France*, Materials Chemistry and Environmental Sustainability, Đa Nang, CMED, p.115-126.