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Quick Test on Methanol in Petrol by Acid Chromotropic

Dũng Nguyễn Tiến[a], Nga Trần Thị Thu[b*], Loan Đoàn Thị Thúy[c]

[a,b,c]*Major, PhD, Environmental Police Department, The People's Police Academy, Vietnam*
[a]*Email: nguyentiendunghvcsnd@gmail.com*
[b]*Email: thungat32@gmail.com*
[c]*Email: thuyloant32@gmail.com*

Abstract

According to calculations by Vietnam Institute of Economic Management, with the development and growth of domestic economy in the next 5 years, the total petroleum demand in the whole country from 2018 to 2022 reaches 6.5 million tons of petrol and 8.5 million tons of diesel oil, on average. Domestic production meets about 92% of A92 gasoline demand, and 82% of A95. An average of 0.8 million tons of petrol per year will be imported from countries into the region such as Singapore, Malaysia, Thailand, South Korea and China to Vietnam. Because A83, A92 gasoline is cheaper than A95, many traders mix methanol with the cheaper, to convert into A95 to increase gasoline octane, changing gasoline quality in Vietnam market [1,2,3]. The authors has successfully developed a reagent capable of detecting methanol in gasoline by the complexing reaction of formaldehyde with chromotropic acid for pinkish purple in acidic medium. By simple analysis, faster time and lower cost, This method helps the authorities to improve the gas quality management in Vietnam. This reseach assess the analytical procedures on determination of methanol in petrol and A92, A95 petrol by the reaction of formaldehyde with chromotropic acid complexes produce purple pink in an acid environment, give results: analytical methods simple, faster analysis time, cost saving. This method hepls to manage quality gasoline in VietNam [3,4].

Keywords: Gasoline; petrol; chromotropic acid; methanol; gasoline octane; quick test.

1. Introduction

In the first eight months of 2018, Vietnam imported more than 8.6 million tons of petrol and oil of all kinds, spent 5.71 billion USD, more 26.4% than in 2017. The largest exporter is Malaysia, accounting for 28 6% of the total petroleum imports (2.23 million tons), South Korea 25.3%, Singapore 23.2%. 70% of those is distributed through retailers, gas stations.

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* Corresponding author.

However, trade frauds in the petroleum business have been quite complicated, causing serious damage to the interests of consumers, as the pressing issue of the society and as a hindrance for enterprises in the process of integration. As a result, it is possible to mix poor quality methanol with gasoline to make profit. Remarkably, methanol is cheaper than gasoline. Some countries have banned the mixture of methanol with gasoline. Currently, the price of industrial methanol in Vietnamese market is less than 10,000 VND per liter. While blending 15% methanol with A83 or A92 gasoline make A95, doubling methanol into gasoline will increase profits. The oil and gas workers must have professional knowledge, they collude with retailers in consuming [1,2,5].

2. Identify the fact

Therefore, to make a practical contribution to the management of petroleum quality in Vietnam, the authors have analyzed the means to add methanol into gasoline and developed a reagent. In addition, we also recommend solutions to improve the quality management of petroleum in the Vietnamese market.

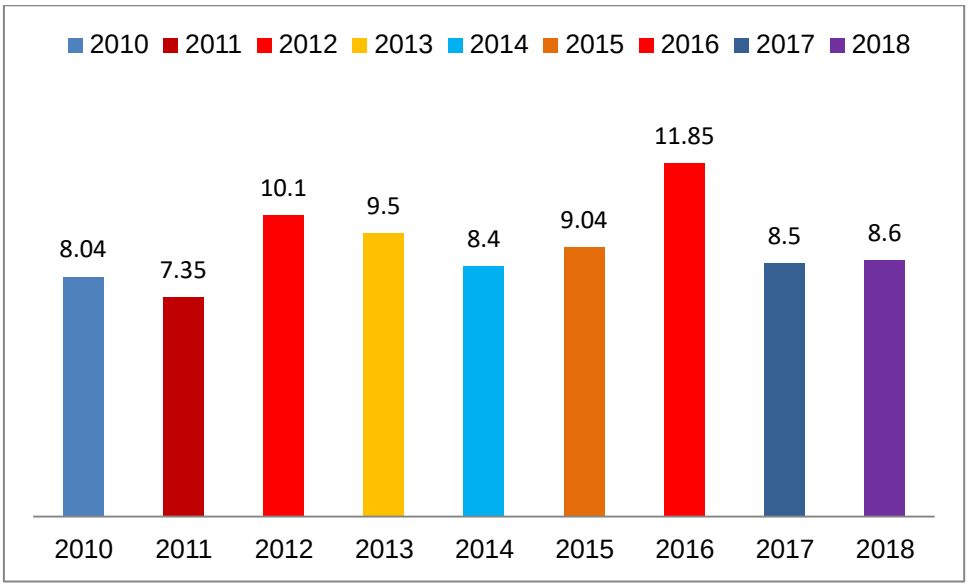

Figure 1: Vietnam's petrol imports (million tons) from June 2010 to June 2018

Tricks of blending methanol with gasoline

Blending methanol at warehouse of large retailers

When importing into general warehouses, the offenders divide gasoline into small gallons, extract gasoline from the tank then add methanol by stirrer to make it soluble enough (more than 15%). By this way, the object can dissolve a large amount of methanol in the gasoline. When the gasoline is stable, its analysis will reach the standard of A95 and the price will be higher. Afterwards, it will be mixed with A95 to dissolve the additives, which makes sub-agents difficult to detect. Another trick is to drain A95 to another tank then add A83, A92 methanol mixed to increase to the same octane index. However, the methanol mixture will make the engine hardly to start. In order o overcome, a flammable substance, called acetone, is added. Acetone is heavier than

air. When the fuel is leaking, acetone gas spreads on the ground. If contact with hot temperature (such as cigarette butts), it may catch fire. This is the reason why the car have parked in the garage for a long time, still burns [1,4,5].

Blending methanol when transporting

During transportation, the objects usually have appointments at the stops, then use the gasoline extraction tools, or reinforce the extra straw at the bottom of the container without opening the clamp. To do this trick, there must be a contact with ones in the warehouse. The loosened seal makes it easy for the driver to open the valve without breaking the seal. Many drivers also design their own tanks inside, when they leave the warehouse, the tanks seem to have enough quantity. After getting out, the driver takes their own petrol tank out for sale. To compensate for the loss, the objects add methanol. During the transportation, the truck's movement will facilitate methanol to dissolve well in gasoline. It can be said that fraudulent quality of gasoline is causing the most serious consequences. The problem is not just the standard deviation that causes engines to operate at low power but also the possibility to catch fire. From 2013, we have witnessed a series of motorbikes burned while running, sometimes not running, and a lot of questions about the quality of gasoline. In many journalists' clips from petrol thefts, there are scenes of adding a liquid to compensate for the amount of petrol that was stolen [4,5].

Blending methanol when preparing for saling at retail outlets

At small retailers, the gasoline amount is only 1000-5000 liters and distributed in a short time. Those who want to increase the volume of gasoline or convert gasoline by mixing with substances difficult to detect such as Mono ethylene glycol. This is a transparent liquid, soluble and difficult to detect when analyzed, low evaporation rate, hygroscopic, boiled at high temperature, light odor. This liquid absorbs a lot of water, what will increase the volume of gasoline and make it more profitable for the seller [1,5]. Another common trick of dealers is that gasoline is added with kerosene along with methanol or similar mixtures. Kerosene has a higher boiled temperature than gasoline (150 to 275 Celsius degree), it is composed of hydrocarbons from C12 to C15, d15 density is 0.78-0.80. When adding kerosene to petrol, the vehicles can run at poor performance but not be burned. While adding more kerosene means more dangerous, such as poor engine performance, environmental pollution. More over, unburned vapor can also cause fire, when meeting the source of heat or sparks [11,12]. Another trick to avoid getting checked by testing RON are the addition of methanol and some oxygenation such as MTBE. It is worth mentioning that the addition of oxygenation will affect the dispersion of fuel vapor and vehicle performance. It changes the reaction before ignition, which reduces the energy content of the fuel. If the objects add methanol to the gasoline at high levels as detected, it will cause the fuel pipe to swell more, the fuel vapor and the oxygenattion to spread out.

3. The impact and consequence

The impact of methanol fuel upon engines and the environment

Long-term use of methanol gasoline, engine and carburetor degraded (due to metal corrosion), joints expansion

may cause fuel leakage, vehicles burned, more severely. In addition, engine warming due to traffic jams may trigger the fire. In spite of being the weak acid, methanol can attack the aluminum oxide layer to form aluminum salts and water. When the protective oxide layer is exhausted, methanol will directly erode aluminum and produce hydrogen. This process continues until the aluminum or the methanol concentration is exhausted. The high aluminum corrosion has a great impact due to the high aluminum percentage in modern engines. Copper, brass, zinc and iron are corroded when the methanol concentration reaches 15% [13,14]. Methanol also causes problems with the elasticity of the engine's fuel supply system. Plastic, such as polyurethane and Buna-N, are greatly affected by methanol, which will catch fire when meeting sparks. This is because of the metal corrosion as well as the elasticity of the fuel tank that car manufacturers prohibit the use of methanol. In particular, the problem of metal corrosion and the alteration in gasoline injection systems is the main cause for the automobile manufacturers not accepting the use of methanol at any rate.

Methanol is produced naturally during the metabolism of many anaerobic bacteria, commonly in the environment. As a result, there is a small fraction of methanol vapor in the atmosphere. In a few days, the methanol is oxidized under the sunlight, forming carbon dioxide and water.

Consequences of methanol consumption for gasoline market

In Vietnam, some gasoline retailers are increasing the octane rating by adding methanol to convert A83 gasoline to A92, A95. This will gain higher profit, but also cause a lot of danger to the engines. At present, Vietnam has not introduced methanol regulations in gasoline. According to the standard 6776 in 2005 on the quality of leaded gasoline, among the 15 compulsory norms, there are not any for methanol criteria [4,5].

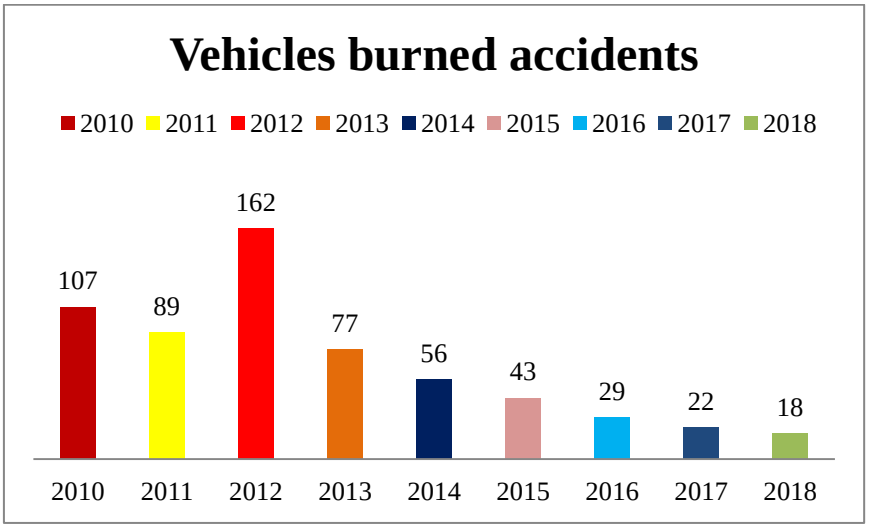

Figure 2: Vehicles burned accidents by using poor quality gasoline in Vietnam from June 2010 to June 2018

The method to discover methanol in gasoline

Scientific basis of the method: In the methanol medium oxidized by potassium permanganate and phosphoric acid, the result is formandehyde, the reaction of formandehyde formed with chromotropic acid gives the pinkish

color. Thus, the determination of methanol through the reaction of formandehyde with chromotropic acid produces a pinkish complex in the acidic medium. To quantify methanol in gasoline, it is possible to measure the optical density of the solution obtained at a wavelength of about 570 nm. Compared to standard methanol concentration, the actual concentration of methanol in the first gas sample can be calculated. The use of chromotropic acid gives color stability, it is easy to observe in the field, in addition, easy-to-find and easy-to-mix. The detection limit can be up to 0.01% Methanol in gasoline. There is no hindrance to normal operations of gasoline agents' business [13,14,15].

The method is developed as follows:

Prepare reagent solution: CH3OH absolute, using standard Merk chemicals. Intermediate Standard solution, CH3OH 10%; Phosphoric acid, H3PO4 5; Potassium permanganate, KMnO4 5%; Sodium bisulfite, NaHSO3 10%; Sulfuric acid, H2SO4 1:1; Chromotropic acid.

Equipment: bottles of 25 ml, 50 ml, 100 ml; pipettes of 1 ml, 2 ml, 5 ml, 10 ml, vials, stove, photometer.

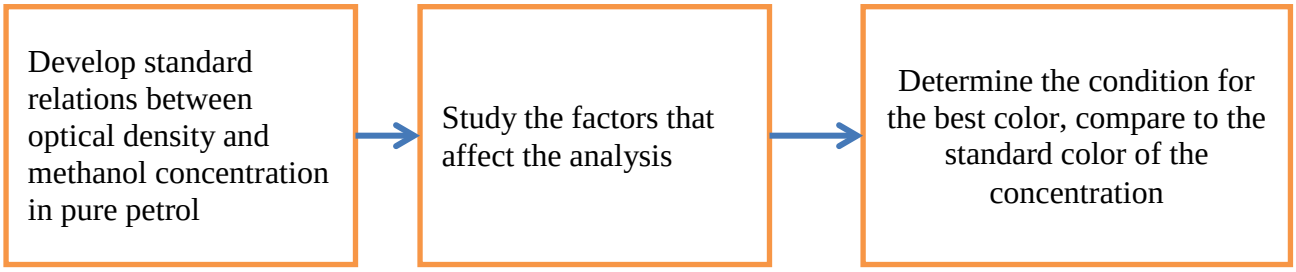

Figure 3: The process of developing a methanol analysis study on gasoline in Vietnam

The discussion

Analyze the methanol concentration in pure gasoline

Develop a benchmark describing the relationships between methanol concentration and optical absorption of the Abs machine

Develop a benchmark according to the following process: Mix methanol substances in the following concentration range:

Table 1: Range of standard methanol solution in pure gasoline

	1	2	3	4	5	6	7
Standard solution (ml)	0,05	0,125	0, 25	0,5	1,25	2,50	5,00
Mark 25 ml							
Concentration at standard range (%)	0,01	0,025	0,05	0,1	0,25	0,5	1,00

Extract 0.5 ml of the standard solution into a 10 ml pipette.

Add 0.5 ml of H3PO4 5% and 0.5 ml of KMnO4 5%, shake it for 1 minute.

Add 1 ml of NaHSO3 10%, shake until the solution completely dissolves.

Add 4 ml of H2SO4 1:1 and a few drops of crushed chromotropic acid, shake well.

Boil at 60 Celsius degree for 15 minutes. Measure the optical density of the purple solution obtained.

Standard benchmark: y = ax + b (x stands for methanol concentration, %)

$$C_{mẫu} = C_{đo} = \frac{Abs - b}{a}(\%)$$

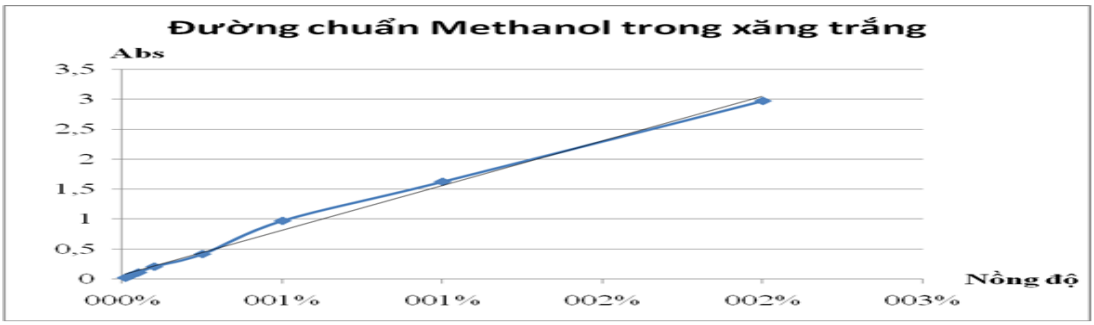

Figure 4: The relationship between methanol concentration in gasoline and optical absorption

Table 2: Methanol Standard Formulation

Nồng độ (%)	0,01	0,025	0,05	0,10	0,25	0,50	1,00	2,00
Abs	0,024	0,057	0,111	0,209	0,418	0,972	1,624	2,971

From the data in Table 2, construct the standard curves as shown in Table 1

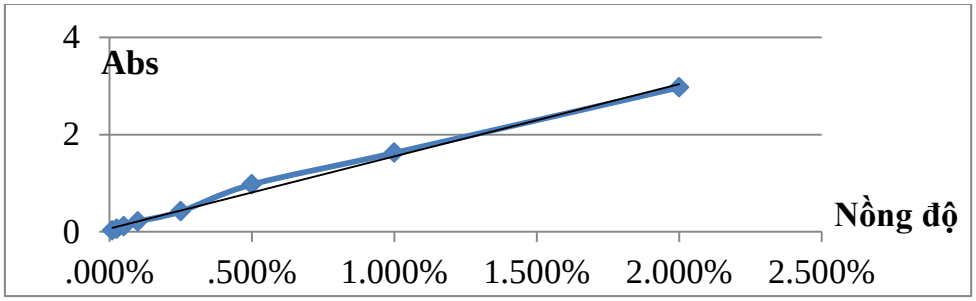

Figure 5: The relationship between methanol concentration in gasoline and optical absorption at concentrations between methanol 0.5% and 2.5%.

The methanol standard in pure gasoline has an equation:

y = 1,4877x + 0,0665

R2 = 0,9943

Factors affecting methanol detection in gasoline

Factors affecting the determination of methanol concentration in gasoline include: Lubricant; Long hydrocarbon;

Effect of additives in gasoline and its exclusion method

Exclusion by distilling A92 gasoline at a temperature of 50-56^{o}C, the additives and gasoline all evaporate. Condensate gasoline to remove additives. The condensated gasoline will be analyzed by procedures with pure petrol.

Exclusion by filtering the A92 gasoline sample through activated charcoal powder. The filtrate will be analyzed by procedures with pure petrol. Gasoline additives are long-chain hydrocarbons, at low temperatures (<0^{o}C). These are in the form of solids or waxes. Lower the temperature of the gasoline to -19°C for 1 hour for the additives to settle down.

Exclusion by removing additives with KMnO4: Extract 0.5 ml of A92 gasoline into test tube, add 0.5 ml of H3PO4 5%. Add 2 ml of KMnO4 5%, shake the tube for 1 minute. Filter precipitate, collect the filtered sample [8,9].

Extract 0.1 ml of the filtrate into a test tube, continue to be analyzed by procedures with pure petrol.

Results of methanol analysis in pure petrol

The effects of boiling temperature

Examine with pure petrol sample containing 0.3% methanol. Prepare 6 test tubes: pure, 20^{o}C, 40^{o}C, 60^{o}C, 80^{o}C, 100^{o}C. Conduct the above procedure.

The results are shown in the following table:

Table 3: The effect of boiling temperature on the optical density

Sample	Pure	20^{o}C	40^{o}C	**60^{o}C**	80^{o}C	100^{o}C
Abs	0	0	0,019	**0,045**	0,043	0,039

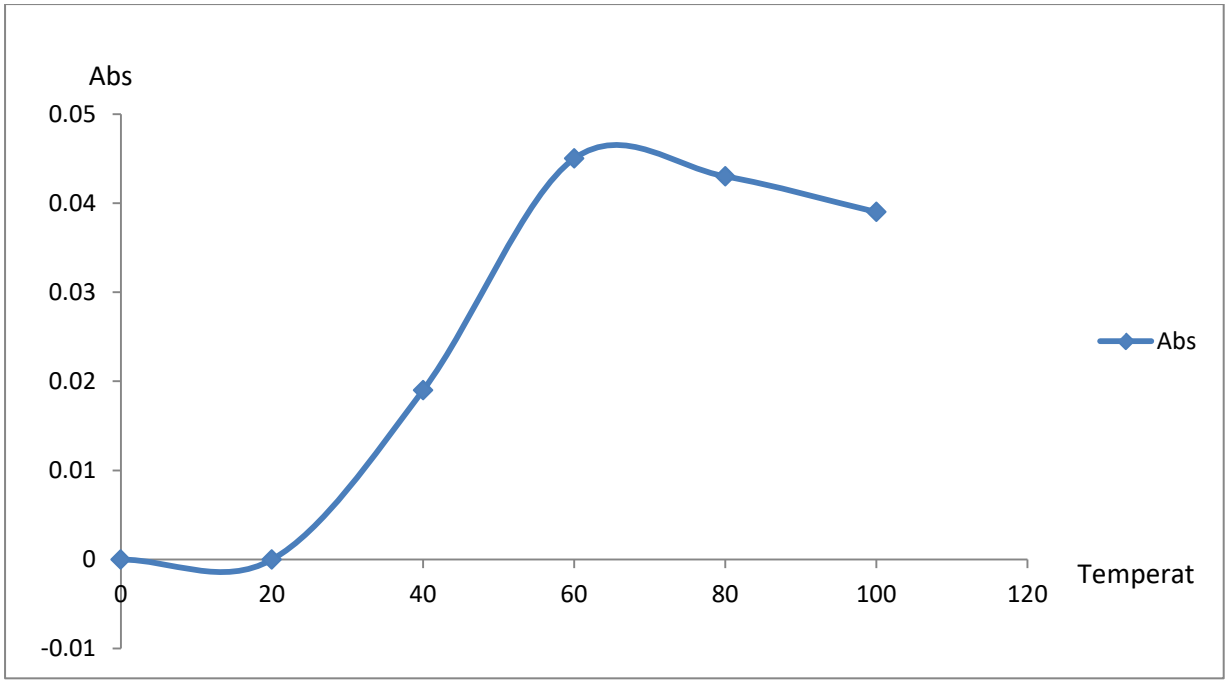

Figure 6: The effect of temperature on absorption of optical density

Based on Table 3, it is found that boiling temperature increases from 20^{o}C to the climax at 60^{o}C and decreas slightly from 80^{o}C. Therefore, the optimum boiling temperature is 60^{o}C.

The effects of boiling time

Carry out a experiment with pure gasoline containing 0.3% methanol. Prepare 6 test tubes, accordingly: pure, 5', 10', 15', 20', 25'. Follow the above procedure.

The results are shown in the following table:

Table 4: The effect of the boiling time on the optical density

Sample	pure	5'	10'	15'	20'	25'
Abs	0	0	0,011	0,023	0,042	0,040

Based on Table 4, the authors find that the optical density increases from 5 minutes to maximal at 20 minutes and unchanged at 25 minutes. Therefore, the optimum boiling time is 20 minutes.

The effects of $KMnO_4$

Examine with pure petrol sample containing 0.3% methanol. Prepare 6 test tubes of $KMnO_4$ at the concentrations, accordingly: pure, 0.3%, 0.6%, 1.2%, 1.5%, 2.0%. Follow the above procedure [11].

The results are shown in the following table:

Table 5: The effect of $KMnO_4$ on the optical density

Sample	Pure	$KMnO_4$ 0,3%	$KMnO_4$ 0,6%	$KMnO_4$ 1,2%	$KMnO_4$ 1,5%	$KMnO_4$ 2%
Abs	0	0,129	0,152	0,118	0,077	0,173

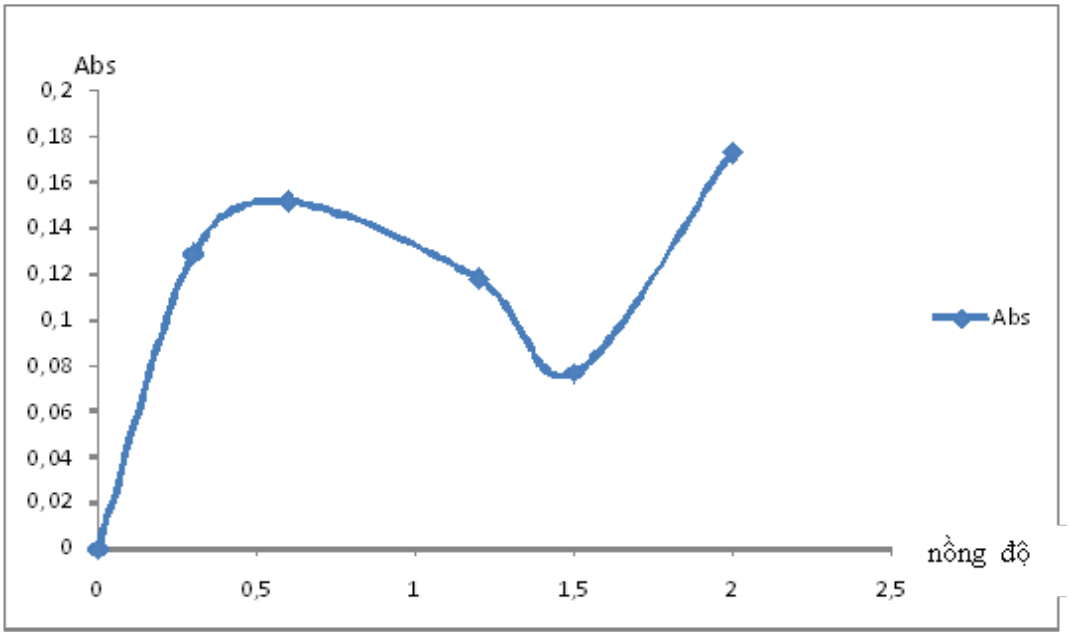

Figure 7: The effects of $KMnO_4$ concentration on reaction

Based on Table 5, it is found that there are two ranges of reaction: from 0.3% to 1.2% and from 1.5 % to >2%.

It is important to divide into smaller ranges.

The effects of $NaHSO_3$

- Examine in 3 conditions:

+ Pure gasoline containing methanol 0.25% and $KMnO_4$ 2%.

+ Pure gasoline containing methanol 0.5% and $KMnO_4$ 2%.

+ Pure gasoline containing methanol 0.25% and $KMnO_4$ 5%.

Pure gasoline containing methanol 0.25% and $KMnO_4$ 2%.

The results are shown in the following table:

Table 6: Optical Density and effectiveness of NaHSO3 with 0.25% Methanol, KMnO4 2%.

Mẫu	Trắng	$NaHSO_3$ 1%	$NaHSO_3$ 2%	$NaHSO_3$ 5%	$NaHSO_3$ 10%	MT
Abs	0	0	0	0,085	0,082	0,089
Hiệu suất	0	0	0	95,5%	92,1%	

At the concentration of NaHSO3 5%, the methanol determination efficiency is best.

3. Solutions

In order to improve the quality of petrol management in Vietnam market, in this article, we give some solutions:

Firstly, to complete legal documents related to state management on petrol quality in the Vietnamese market

Currently, the Prime Minister has requests the Ministry of Industry and Trade to supplement some articles of the draft decree. Accordingly, the Ministry of Industry and Trade will preside over the inter-sectoral group to run the price stabilization fund. The Ministry of Finance shall perform the function of state management over prices. At the same time, assuming responsibility for setting up and the price stabilization fund . The range of prices for gasoline retailing is adjusted to three levels: below or equal to 3%, from over 3% to 7% and above 7%. It clearly determines the competence of price adjustment and the form of management corresponding to each level of adjustment. Specifically, key traders are entitled to decide the price increase within the first level, the second level must to be reported to the Ministries; The final level (over 7%) shall be reported to the Prime Minister [5,6].

In the world, many standards of quality management have been issued such as TQM, ISO 9000, HCCP, GMP, ISO 14000... ISO 9001:2000's regulations on quality management, meets the requirements of customers and is suitable for enterprises in Vietnam. If the state obliges importers and the first-class retailers to apply this standard, it will minimize the loss to fuel consumers [7,8].

Secondly, to improve the responsibility of state management system on petroleum business in Vietnam

To compulsorily apply the ISO 9001:2000 system on quality management in importing and trading petroleum in Vietnam market. In particular, to increase competence for the authorities in handling with violations of petroleum business.

Thirdly, to intensify the scientific research on quality control technique

To find out the technical solutions for inspecting petrol dealers. In addition, it is necessary to have specialized transportation monitors for transit, storage, transport and distribution in the petrol business.

Fourthly, to raise the public's awareness in preventing fuel law violations by propaganda

To improve the quality of the media messages. The propaganda materials should focus on guiding the behavior, suitable to each object (producer, processor, trader, consumer...).

Fifthly, to strengthen the relationship with the related agencies in crime prevention in petrol business.

To coordinate in the inspection on petrol import and trading. To organize dissemination and education activities. To guide the implementation of legal provisions on the handling of law violations in each stage: Manufacturing, processing, trading, import and export, distribution at agents in different levels. It is necessary to define the principles, responsibilities and obligations for the subjects participating in the coordination; specifically, to severely fine for any violations. To coordinatte with other functional agencies in socializing the prevention in petrol business, in controlling petrol trading activities in the market [15,16].

4. Conclusion

The reagent can detect methanol in gasoline at a concentration of 0.01%. The test kit consists of five tubes prepared from 1 to 5:

Tube 0 : The petrol sample needs to be analyzed;

Tube 1: The sample after being extracted, adding 0.2 ml of concentrated H3PO4 (number 1);

Tube 2 : 0.2 ml of KMnO4 (number 2);

Tube 3 : 0,2 ml of NaHSO3 (number 3);

Tube 4: 0,3 ml of H2SO4 and 0,1 ml of Chromotropic Acid (number 4);

Figure 8: The result of experiment on methanol detecting in Vietnam

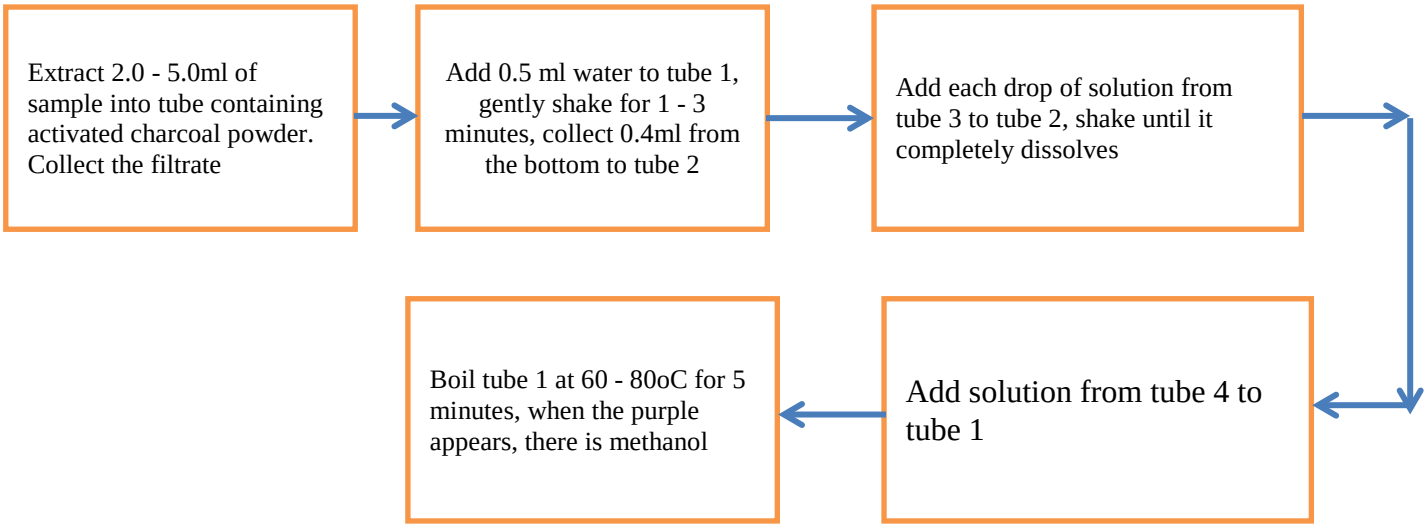

Figure 9: Unauthorized methanol discovery process in gasoline.

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