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IMPACT OF ANTIOXIDANTS ON THE STABILITY OF DIESEL FUEL



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งานวิจัยนี้เป็นการศึกษาถึงผลกระทบของสารแอนติออกซิแดนซ์ต่อเสถียรภาพของน้ำมันดีเซล โดยดัดแปลงวิธีมาตรฐานเพื่อทดสอบหาเสถียรภาพของน้ำมันดีเซลที่มีสารแอนติออกซิแดนซ์ผสมอยู่ เร่งให้เกิดปฏิกิริยาออกซิเดชันภายในเครื่องมีระบบปิดซึ่งอ้อมตัวด้วยออกซิเจนที่มีความดันประมาณ 690 kPa (100 psi) ประเมินเสถียรภาพของน้ำมันตัวอย่างจากระยะเวลาในการเกิดปฏิกิริยา ปริมาณสารเปอร์ออกไซด์ ปริมาณสารไม่ละลายที่เกิดขึ้น และความเข้มของสีน้ำมันที่เปลี่ยนแปลงไป โดยการแปรค่าอุณหภูมิทดสอบในช่วง 25-100 องศาเซลเซียส ระยะเวลาในการเกิดปฏิกิริยา ชนิดและความเข้มข้นของสารแอนติออกซิแดนซ์ ปริมาณกำมะถัน และไนโตรเจนเฮเทอโรอะตอม ปริมาณสารอะโรมาติก และองค์ประกอบของน้ำมันดีเซล รวมทั้งศึกษาถึงผลกระทบที่เกิดจากภาวะแวดล้อมในการเก็บรักษาที่แตกต่างกัน

ผลการศึกษาพบว่าสารแอนติออกซิแดนซ์สามารถป้องกันการเสื่อมสภาพของน้ำมันดีเซลได้ โดยการเพิ่มระยะเวลาในการเกิดปฏิกิริยา ลดการเกิดสารเปอร์ออกไซด์ ชะลอการเกิดสารที่ไม่ละลายและการเปลี่ยนแปลงสีของน้ำมันดีเซลหลังเกิดปฏิกิริยา และพบว่ามี 4 ปัจจัยที่สำคัญที่ทำให้ น้ำมันดีเซลไม่เสถียรคือ องค์ประกอบที่ได้จากกระบวนการทำให้โมเลกุลแตกตัว ซึ่งประกอบด้วยสารประกอบอะโรมาติกและสารประกอบประเภทไม่อิ่มตัวเป็นหลัก ปริมาณเฮเทอโรอะตอม อุณหภูมิและภาวะในการเก็บรักษา ถึงแม้ว่าสารแอนติออกซิแดนซ์มีผลในการยับยั้งปฏิกิริยาออกซิเดชันให้เกิดช้าลงได้ แต่อย่างไรก็ตามมันจะทำหน้าที่ในการยับยั้งปฏิกิริยาโดยมีกลไกในการเกิดปฏิกิริยาที่แตกต่างกัน สารแอนติออกซิแดนซ์ประเภทฟีนอลและชนิดอื่นๆ หากต้องการเพิ่มประสิทธิภาพของสารแอนติออกซิแดนซ์ในการยับยั้งปฏิกิริยาออกซิเดชัน เพื่อป้องกันการเสื่อมสภาพของน้ำมันดีเซลควรใช้สารเติมแต่งประเภทผสม และพบว่าปริมาณสารแอนติออกซิแดนซ์ที่เหมาะสมสำหรับเก็บรักษาน้ำมันดีเซลเป็นเวลานาน 1 ปี ที่ภาวะปกติคือ 40-60 มิลลิกรัมต่อลิตร

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The effect of antioxidants on the stability of diesel fuel in this research was performed by using modified method to determine stability of diesel fuel blended with antioxidants. The fuel samples were oxidized in an oxidation bomb with fixed amount of oxygen pressure at 690 kPa. The stability of diesel fuel was characterized by induction period, peroxide value, total insoluble and color development. Investigations were operated by varying in temperature at 25-100 ° C, type and concentration of antioxidants, heteroatom, aromatic content, and component distribution. Additionally, the effects on storage condition were also studied.

Antioxidants were found to improve fuel stability from degradation by increasing of induction period, decreasing peroxide value, prevention of insoluble formation and color development after oxidation. There were four significant factors that led to instability of diesel fuel that were the percentage of hydrocracked fraction, amount of heteroatom, temperature and storage conditions. Although antioxidants could retard oxidation, however they acted as antioxidant by different mechanism. Amine type was more effective in delay oxidation better than phenol type and others. However the requirement of synergistic benefit to improve stability would be possible with the combination of additives. The optimum dosage of antioxidants to be used for 1 year storage at normal storage condition was about 40-60 mg/l.

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ABBREVIATIONS

HSD	=	High Speed Diesel
HGO	=	Heavy Gas Oil
LGO	=	Light Gas Oil
HCGO	=	Hydrocracking Gas Oil
ADO	=	Automotive Diesel Oil
°C	=	degree Celsius
psi	=	pound per square inches
mg	=	milligramme
ml	=	millilitre
h	=	hour
N	=	Nitrogen
S	=	Sulfur
PV	=	Peroxide Value
mg/l	=	milligram per litre
kPa	=	kilopascal
O ₂	=	oxygen gas
%	=	percent
vol	=	volume
cSt	=	centistokes
s	=	second
min	=	minute
L	=	litre

CHAPTER I

INTRODUCTION

One of the major problems encountered in the petroleum industry is the deterioration of middle distillate fuel oils (diesel fuel) on storage. The deterioration products can cause deposits (sediment formation) that in turn lead to filter and injector plugging.

The stability properties of diesel fuel are highly dependent on the crude oil source, severity of processing whether additional refinery treatment has been carried out and the composition of produced distillate fuels because blends of fuels from various sources may interact to give stability properties worse than expected based on the characteristics of the individual fraction of fuel such as heavy gas oil, light gas oil, hydrocracked gas oil.

Normally, produced diesel fuels have adequate stability properties to withstand normal storage without the formation of insoluble degradation products but in recent years the problem of stability of diesel fuels has become more pronounced with the increasing use of cracked products in diesel oil formulation. These cracked products induce formation of sediment and color development in fuels at typical storage conditions. Since hydrotreatment removes many polar species that are natural antioxidants, refined fuels usually oxidize more rapidly and require the addition of synthetic antioxidants to improve stability during storage [1]

Fuel degradation products in diesel fuels are formed in fuels during extended storage. Insoluble degradation products may combine with other fuel

contaminants to reinforce deleterious effects. Soluble degradation products are less volatile than fuel and may carbonize to form in fuel due to complex interactions and oxidation of small amounts of olefinic, sulfurous, oxygenated and nitrogenous compounds present in fuels. The formation of degradation products may be catalyzed by dissolved metals especially copper salts [2].

The three main processes generally used to improve fuel stability are the removal of precursors that would cause deterioration, modification of chemical composition or physical properties, and elimination of the effects of sediment precursors. These can be achieved by hydrotreating, caustic scrubbing, acid or clay treatment and the use of additives.

It is estimated that 70 to 80 percent of domestic heating oil sold today contains one or more additive to provide improved storage, thermal stability and oxidation stability of fuels including middle distillate oil (diesel fuel)[3].



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The objective of this research

The objectives of this research were as the following:

1. To investigate the impact of antioxidants on the stability of diesel fuel.
2. To prevent the deterioration from oxidation at various storage conditions including sediment formation and color development of diesel fuel.
3. To study the suitable type and optimum dosage of antioxidant additives to be used to improve stability of diesel fuel.

The scope of this research

1. Selection of the method for determination of oxidation stability of diesel fuels.
2. Determination of oxidation stability of diesel fuel by comparing chemical and physical properties of these fuel that were incorporated antioxidant additives with those of the neat fuels by the following procedures, such as the induction period at each tested condition, the color development after oxidation at the various tested conditions, the total insoluble (deposit and sediment formation) after stressing at various temperatures and various reaction times, and peroxide value(PV) before and after oxidation with oxygen at pressure of 690 kPa (100 psi) in the oxidation equipment at various tested conditions .

3. Investigation of the effects of heteroatoms which were with sulfur and nitrogen content and aromatic in correlation with its density and fuel compositions on the stability of diesel fuel.
4. Investigation of types the of antioxidant additives from various suppliers on the stability of diesel fuel vary severity of processing with under different oxidizing conditions.
5. Evaluation of the impact of antioxidant additives from both single and combination of additives (package) on the stability of diesel fuel.
6. Evaluation of the optimum dosage of antioxidant additives to be used to improve stability of diesel fuel oil without forming degradation products.



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CHAPTER II

THEORETICAL CONSIDERATION

The ability of a diesel fuel to remain unchanged during the period between its manufacture and its eventual use in an engine is an important quality requirement. Most commercial deliveries of diesel fuel are consumed within a few weeks of leaving the refinery and the likelihood of degradation is small. However, it is the policy of many governments to lay down stocks of all types of fuel for use in emergencies. These strategic reserves are normally subject to periodic turnover. Quantities will be withdrawn for use and replaced by newer batches at intervals, but it is possible that some fuels may be in extended storage for periods of more than one year before turnover.

Changes that can occur with an unstable fuel are due to oxidative breakdown, resulting in the formation of sediments and gums. These reaction products may degrade the color of the fuel but, more seriously, could also cause engine operating problems due to blockage filters or deposits on the injectors and in the combustion chamber [4].

2.1. Theory of oxidation

Oxidation is a major chemical process causing adherent and filterable insoluble to form. These reactions may be promoted by other contaminants such as dissolved metal salts example copper, chromium. Oxidation reaction is leading to fuel degradation during storage. Storage stability varies enormously due to

refinery feedstock source (crude oil or otherwise) and type of processing used to produce component in the finished fuel. Because the chemical reactions leading to formation of sediment (and color) vary depending on the type and amount of unstable materials such as olefinic, sulfurous, oxygenate and nitrogenous compound [5].

The composition and stability properties of distillate fuels produced at specific refineries may be different. Blends of fuels from various sources (straight-run, hydrocracking gas oil, heavy gas oil) may interact to give stability properties worse than expected based on the characteristics of the individual fuels.

Oxidation stability problems may occur with excessive storage time, as is sometimes required for military fuels. For storage at high ambient temperatures, inert gas blanketing (often nitrogen) is sometimes used to minimize oxidation of the fuel.

Diesel fuel can oxidize during storage giving rise to the formation of gums and gum precursors that can cause deposit formation in engine and seriously influence their performance, therefore may need some special processing or the use of antioxidants.

Oxidation is the initial step in fuel degradation. The self-accelerating oxidation of hydrocarbons at low temperature is called "autoxidation". Autoxidation chain mechanism has been proposed to describe fuel oxidation and deposition behavior. The actual mechanism of autoxidation, including possible initiation sources and back reactions, is significantly more complicated consideration as a chain breaking mechanism, starting with the basic chemistry of

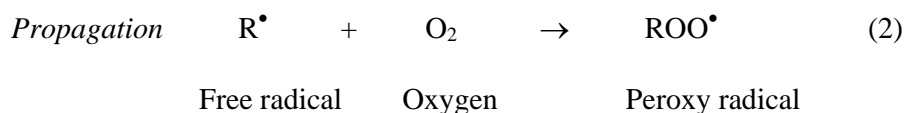
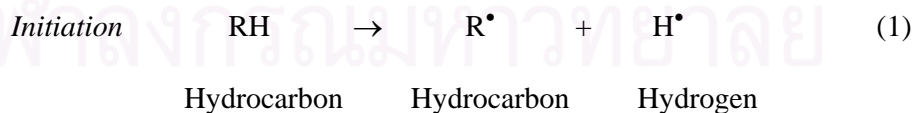
the autoxidation chain. Its initial stage is characterized by slow reaction with oxygen followed by a phase of increased conversion until the process comes to a standstill. The degradation is driven by an autocatalytic reaction, which can be described by the well-established free radical mechanism [6].

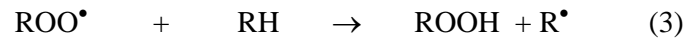
The hydrocarbon oxidation process takes place in four stages:

- Initiation of the radical chain reaction
- Propagation of the radical chain reaction
- Chain branching
- Termination of the radical chain reaction

In the initiation stage, a hydrocarbon molecule loses an atom of hydrogen to give a hydrocarbon free radical. In the propagation stage, a hydrocarbon free radical reacts with a molecule of oxygen to form a peroxy radical. The peroxy radical then reacts with a fresh hydrocarbon molecule to form a hydroperoxide molecule and new hydrocarbon free radical. In the chain branching stage, hydroperoxides may be cleaved homolytically or may react via bimolecular mechanism to yield an alkoxy and a hydroxy radical. Finally, in the termination stage, two free radicals interact to produce one or more stable molecules.

The four stages are presented as follows

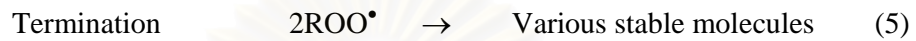




Peroxy radical Hydrocarbon Hydroperoxide



Hydroperoxide



The summary of autoxidation chain mechanism is shown in figure 2-1. [7]

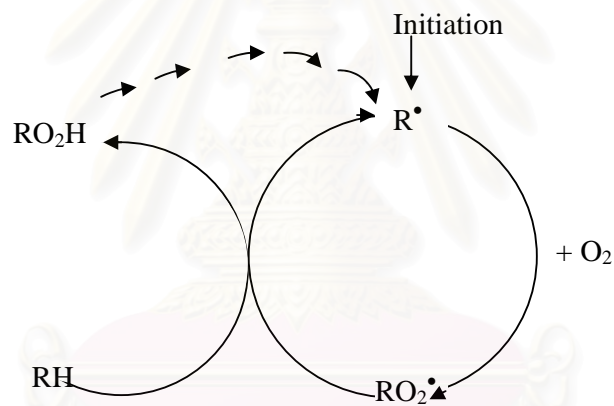


Figure 2-1 :Autoxidation chain mechanism of Fuels

An initiation reaction results in the formation of an alkyl radical, R^\bullet . The alkyl radical reacts with dissolved oxygen, O_2 to form an alkyl peroxy radical, RO_2^\bullet . The alkylperoxy radical reacts with another fuel molecule, RH , to generate a hydroperoxide, RO_2H , and another alkyl radical, R^\bullet , thus propagating the chain mechanism. Autoacceleration occurs when the hydroperoxide decomposes to

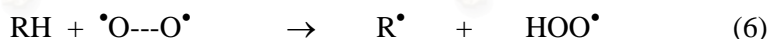
form two radicals: RO^\bullet and $^\bullet\text{OH}$. The multiple arrows indicate that these two radicals further react to contribute to the pool of alkyl radicals, R^\bullet .

Following to chain mechanism above. reaction (5), termination, has been written as the recombination of RO_2^\bullet rather than the R^\bullet because reaction (2) proceeds with no activation energy, whereas reaction (3) has a significant activation energy for most hydrocarbons. Therefore reaction (3) is the slow step and RO_2^\bullet is the major radical species. A hydrocarbon is easily oxidized if reaction(3) proceeds with a small activation energy. This requires a weak carbon – hydrogen bond [8].

Each of the stages will now that considered in more detail.

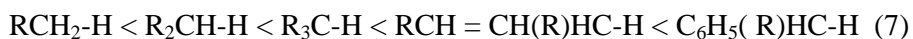
2.1.1. Initiation of the radical chain reaction

The oxygen can react directly with a hydrocarbon. The mechanism is based on the fact that the oxygen molecule itself behaves like a diradical, because it has two unpaired electrons. As a result, it will attack a hydrocarbon and remove hydrogen.

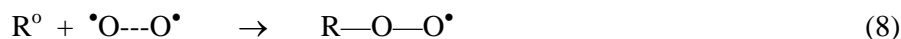


Hydroperoxy radical

The site of the oxygen attack is determined by the strength of the C–H bond, and the reactivity for hydrocarbon abstraction increases in the following order:



The hydroperoxy radical can also attack a hydrocarbon molecule to produce an alkyl hydroperoxide.



The hydroperoxy radical can also attack a hydrocarbon molecule to produce an alkyl hydroperoxide.



The initiation stage of low-temperature oxidation is encouraged by higher temperature.

2.1.2 Propagation of the radical chain reaction.

The simplest propagation mechanism is shown in equation (2) and (3).

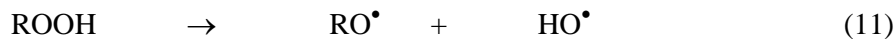
Reaction (2) is extremely fast and has very low activation energy. The rate of reaction of carbon centered radicals with oxygen depends on the type of substituents attached to the C-atom and increases in the following order:



The next step in equation (3) produces an alkyl hydroperoxide ROOH and an alkyl radical R° which can again react with oxygen according to reaction (2). The rate of reaction of step (3) is slow.

2.1.3 Chain branching

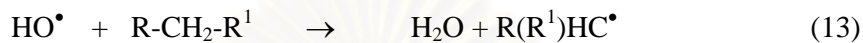
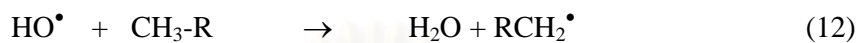
During the early stage of autoxidation various types of hydroperoxides are generated. At low concentrations, they may be cleaved homolytically to yield an alkoxy and a hydroxy radical:



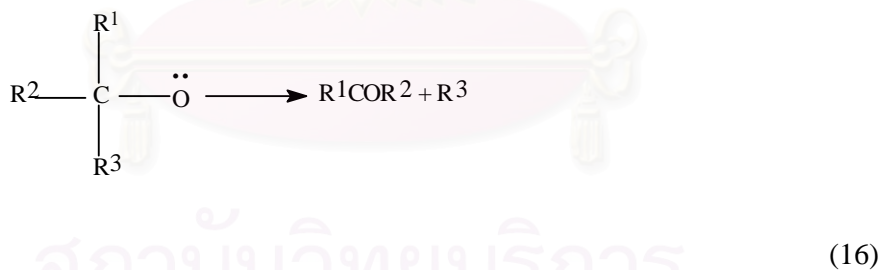
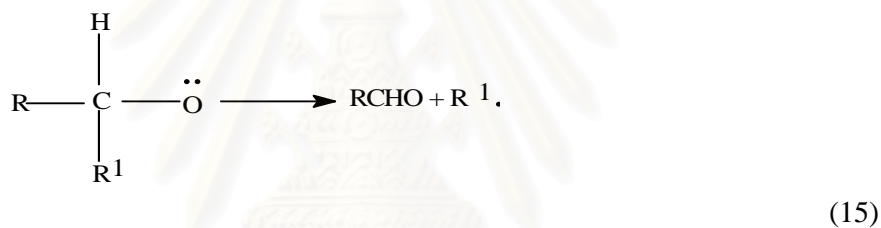
Alkoxy radical Hydroxy radical

However, this process rarely occurs because of high activation energy.

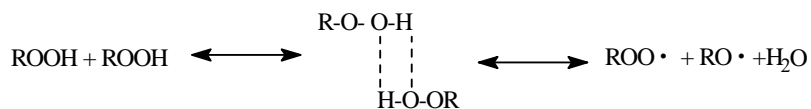
Hence reaction (11) only plays a significant role at higher temperatures or under catalysed conditions. Once formed, hydroxy and especially primary alkoxy radicals are so active that they abstract hydrogen atoms in non-selective reactions:



Secondary and tertiary alkoxy radicals prefer to form aldehydes and ketone:



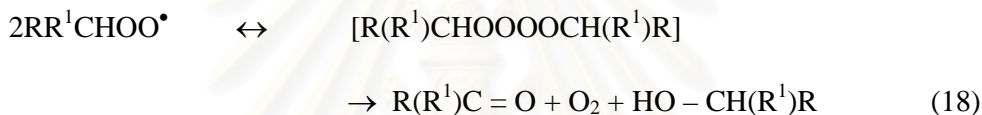
At high concentrations, i.e. at an advanced state of oxidation, hydroperoxides may react via a bimolecular mechanism:



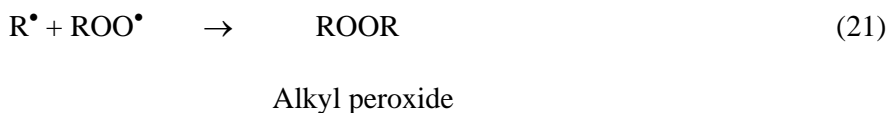
As a consequence of hydroperoxide accumulation and subsequent cleavage, the concentration of reactive free radicals initiating new chains increase. The time from the beginning of the oxidation to the autocatalytic phase of the autoxidation is called the 'induction period'.

2.1.4 Termination of the radical chain reaction

The basic termination stage is shown in equation (5), the combination of radical species (such as peroxy radicals) to yield unreactive species (such as ketones and alcohols):



In this example, primary and secondary peroxy radicals form intermediates, which disproportionate to non-radical degradation products. In contrast, tertiary peroxy radicals may either combine to give di-tertiary alkyl peroxides or undergo a cleavage reaction leading to ketones and alkyl radicals. Furthermore, many alternative terminations are possible in which any pair of free radicals combine together to form a larger stable molecule. Examples are



Chain termination can also take place by reaction of a free radical with an unsaturated molecule (olefin) or aromatic molecule to produce a large free radical.



Certain non-hydrocarbons, such as hindered phenols or amines, are readily attacked by free alkyl radicals to form stable compounds.

The concentration of radicals can be calculated by equations (1)–(3) on the assumption that the concentrations of R^{\bullet} and RO_2^{\bullet} radicals are constant in time; R_i is the rate of formation of radicals in the initiation reaction (A). This is known as the stationary – state hypothesis (SSH) [9].

$$d[R^{\bullet}]/dt = R_i - k_2[R^{\bullet}][O_2] + k_3[RO_2^{\bullet}][RH] = 0 \quad (1)$$

$$d[RO_2^{\bullet}]/dt = k_2[R^{\bullet}][O_2] - k_3[RO_2^{\bullet}][RH] - 2k_5[RO_2^{\bullet}]^2 = 0 \quad (2)$$

$$[RO_2^{\bullet}] = (R_i/2k_5)^{0.5} \quad (3)$$

Using the concentration of RO_2^{\bullet} from Equation (3) and the steady state Equation (1), the rate of oxygen consumption can be written

$$\begin{aligned} -\frac{d[O_2]}{dt} &= k_2[R^{\bullet}][O_2] = R_i + k_3[RO_2^{\bullet}][RH] \\ &= R_i + k_3(R_i/2k_5)^{0.5}[RH] \\ &\cong k_3(R_i/2k_5)^{0.5}[RH] \end{aligned}$$

Therefore the peroxidation of hydrocarbons by the chain mechanism proceeds without any dependence on the oxygen concentration.

Evaluation of the oxidative stability of diesel fuel is an old and complex topic still, a generally applicable, fully satisfactory method is yet to emerge. For oil sample, it is important to know both the current oxidative status and relative potential to undergo oxidative degradation. A single measurement of the peroxide

content (Peroxide value, PV) can be used as an index of current oxidation status only if peroxides formed are stable enough so that they do not decompose after formation. Oxidative stability assessment based on a single PV measurement is often used to estimate the shelf life of a product (Time for the actual field storage; storage period). Because of the magnitude of the peroxide value is an indication of the quantity of oxidizing constituents present. Deterioration of diesel fuel results in the formation of peroxides and other oxygen – carrying compounds. The peroxide value those compounds that will oxidize potassium iodide.

Even if peroxide value may provide an indication of the current oxidative status it can give no information on the relative potential of a sample to oxidize. Broadly, there are two approaches to determine potential oxidative stability. The first is to evaluate the induction period observed before significant production of peroxides (or secondary products) begins. The induction period is very dependent on the conditions of the oxidation experiment. The induction period can also be monitored by monitoring the consumption of oxygen. In our test, the sample is heated (oxidized) at the temperature of test in a closed vessel and pressure decrease, due to the consumption of oxygen, is monitored. Reaction is limited by the fixed amount of O_2 present in air-saturated fuel. An automate embodiment of this is the oxidograph in which the sample is heated in a reaction vessel under 100 % oxygen (pressure of 690 kPa (100 psi), and the induction period is determined from a sudden pressure decrease.

Another official method that measures the induction period is the oil stability index (OSI) method, A stream of purified air is passed through a hot fuel

sample, and the effluent air is bubbled through deionized water. The conductivity of the water is continuously monitored. As the final oxidation products, volatile carboxylic acid are formed in fuel sample. These are flushed out by the flowing air and are collected in the water, resulting in an increase in the conductivity. The time of the onset of the major conductivity rise of the water is obtained by tangential extrapolation

As such, the oxidation experiment must be carried out according to some set protocol. The most commonly used method is called the active oxygen method (AOM), promulgated by the American Oil Chemists Society. This method has been largely unchanged in the past five decades.

The induction period may be used as an indication of the tendency of diesel fuel to form sediment (insoluble) in storage. It should be recognized, however that its correlation with the formation of sediment in storage may vary markedly under different storage.

The other principal option for assessing potential oxidative stability is monitoring the rate of peroxide formation or oxygen consumption, versions of the AOM that attempt to measure the oxidative stability on a shorter period involve a single measurement of the PV after 4 or 20 h of aeration. In oxygen consumption methods, the sample is sealed under air or oxygen and stored at a constant temperature. The oxygen concentration in the head space is monitored by periodically withdrawing small samples through multiply sealed septa affixed to the container and analyzing them by gas chromatography several different types of samples have been analyzed [10].

2.2. Theory of sediment formation in fuels

The possibility of long term storage of diesel fuel is determined by their physical and chemical stability. To evaluate chemical stability the following are studied acid number, oxygen absorption optical density, amount of insoluble gum, amount of total insoluble, etc. The last two parameters are considered the most important factors in the stability of diesel fuels [11].

Normally, produced fuels have adequate stability properties to withstand normal storage without the formation of trouble - some amounts of insoluble degradation products. Fuel that are to be stored for prolonged periods should be avoid formation of sediments, which can overload filters or plug combustor nozzles or injectors [2].

2.3. Color development

The production of distillate fraction by hydrocracking heavy oil residue has been the subject of several studies performed in Petroleum Authority of Thailand laboratory. Under some conditions, the diesel fraction from hydrocracking has been observed to change color, from a clear transparent hue when it is first produced to a dark brown or black after several days of storage. This degradation in color is not generally accompanied by any apparent change in the other measurable physical or chemical properties. While the dark color does not affect diesel fuel performance, it is undesirable because consumers tend to associate dark colors with poor fuel grades.

Color degradation is not the only fuel instability phenomenon. Several reviews on fuel instability emphasizing sediment formation have been published. Deposit on heat exchange surface and formation of both soluble and insoluble gums are other types of fuel instability. Because storage sediment has been studied more extensively than other instabilities, more of those studies are available to compare with color degradation [12].

Oxidation is the initial step in fuel degradation. Although saturated hydrocarbons autoxidize more slowly than either olefins or molecules with benzyl C – H structures which react particularly rapidly, some nitrogen containing and oxygen containing molecules autoxidized readily to hydroperoxides. Subsequently, the products of oxidation can combine with either polar compounds or neutral compounds in the fuel via chemical bonding (including hydrogen bonding) to form sediment [13].

2.4. Diesel fuel additives [14]

2.4.1 Definition of additives

Additives are chemicals introduced in very small proportions to the fuel to improve performance, enhance it in respect of its desirable characteristics and to reduce the effects of its undesirable ones.

2.4.2 Diesel fuel additives

Until the 1970s there was little or no use of additives in automotive diesel fuel. The product manufactured at most refineries around the world was generally a blend of straight-run atmospheric distillate components and, apart

from sulfur content, the specification points could be met without the need for further processing or the use of additives. In the U.S., where the enormous gasoline market had necessitated a high level of downstream conversion to yield more gasoline components, some cracked gas oils went into diesel fuel.

Routine use of diesel fuel additives effectively started in the late 1960s in Europe, with the introduction of cold flow improvers. With the largest proportion of diesel-powered road vehicles of any world region, the growth in demand for diesel fuel was starting to pose problems for the refining industry. The supply situation was further aggravated by the crude oil price rises during the 1970s. Although total demand for petroleum products went down, refiners had to increase the yield of diesel fuel while reducing crude throughput. The use of flow improvers enabled the refiner to produce more diesel fuel by cutting deeper into the crude oil and using the additive to restore the cold properties of the fuel.

Other additive types are now being used in diesel fuel, as more refineries have been obliged to move towards the typical pattern in the U.S., with downstream conversion units to increase the yield of “ clean ” products by cracking the fractions used for heavy fuel oil, for which there is a decreasing demand.

More low-cetane material is being diverted into automotive diesel fuel because it can no longer be absorbed by the shrinking market for domestic heating oil. This necessitates occasional use of an ignition improver to bring the cetane number on specification.

An additional factor influencing the trends in additive use is a growing awareness of the need for fuel product differentiation in the marketplace. It is common practice in many countries for oil companies to exchange and rebrand products to keep down the costs of fuel transportation, the exchanged product being accepted on the basis of an agreed specification and marketed as such. Nowadays, further additive treatment may be made before an exchanged fuel is sold, in order to support the marketing company's advertising claims for a product of superior quality to those of its competitors. This practice has been widely adopted in Europe and other parts of the world.

2.4.2.1 Stability Improvers

Antioxidants, stabilizers and metal deactivators are types of additive which are sometimes used in diesel fuels considered to be prone to oxidative or thermal instability due to the components used for their preparation. If oxidation takes place, engine operation could be affected due to filter blocking or gummy deposits in the injection system and on injector nozzles. In some countries a fuel might be unacceptable for marketing as automotive diesel if the maximum color specification is exceeded.

Cracked gas oils have predominantly been used as blend stocks for distillate and residual heating fuels but, with those markets declining, more cracked gas oil is being diverted into diesel fuel. Distillates from cracking operations are more olefinic than those from atmospheric distillation, and contain more nitrogen compounds. As a result, they are less stable, being prone to oxidation by free-radical reactions. This is the main reason why oxidation

stability limits are being introduced into more diesel fuel specifications. Very complex reactions that cause degradation of the fuel proceed in a series of steps to give rise to the formation of high molecular weight, non-radical molecules.

Two classes of compound that are produced during storage under ambient conditions have been identified as linked indole and phenalene ring systems. Such compounds are soluble in diesel fuel but, if allowed to react with acids, form an insoluble sediment virtually indistinguishable from the polar, highly colored part of naturally formed sediment.

2.4.2.1.1 Antioxidants and stabilizers

Antioxidants used in diesel fuels are usually hindered phenols that prevent high-temperature gum-forming reactions. Stabilizers are amines or other nitrogen-containing basic compounds that prevent sediment formation at ambient temperature by interfering with acid-base reactions. These additive types are not normally used in diesel fuel prepared from straight-run components but, if it contains cracked gas oil, protection may be desirable, especially if the fuel is likely to be in storage for a lengthy period.

The same types of antioxidant are used in diesel fuels and gasoline to prevent high-temperature reactions, but stabilizer additives are more specific in their action and need to be selected to suit the particular fuel to be treated.

2.5 Literature Reviews

It has long been known that oxygen consumption is an important first step in the formation of deposit in fuels. Many mechanisms have been proposed

to account for deposit formation. Most start with the autoxidation chain cycle and assume that the products of oxidation initiate the formation of deposits.

G.F.Bol Shakov (1970), [15] stated that condensation reaction of peroxides and other oxidized products are responsible for solid formation.

R.H. Chark and L.Smith (1988), [16] defined the initial stage of deposit formation as oxidation via a free – radical chain mechanism and second stage as the reaction of trace compounds with the oxidation products. They proposed a simplified two step model. The first step is the production of peroxides and other oxidized intermediate materials. In the second step, these products react with sulfur and nitrogen containing compounds to form deposit materials.

Zh.D.Kalichin, SI.K. Ivanove, S.K.Taneilyan, M.I.Boneva, P.T.Georgier, A. Ivanor and K. Kanorier (1991), [17] studied chemical stability of diesel fuels and sediment formation therein at elevated temperature. They showed that there are two basic processes leading to the formation of total insoluble in diesel fuels which are the formation of gum as a result of thermal and chemical processes in the absence of atmospheric oxygen and oxidation of hydrocarbons by atmospheric oxygen. Otherwise comparing the experimental data and values of initiation rate constant for total insoluble formation calculated by the kinetic approach showed that the process not just a polymerization reaction and sulfur content is significant influence on the formation of total insoluble.

R. N. Hazlett (1991), [18] proposed that hydroperoxides are the alkoxy free radical that forms from the decomposition of hydroperoxides. He listed three key criteria for deposit formation that any proposed mechanism must meet:

1. Dissolved oxygen initiates the process.
2. Heteroatom-containing molecules should play an important role.
3. Only a small amount of the fuel is involved in the deposit formation process.

S. P. Heneghan and S. Zabarnick(1992), [19] proposed a fourth criterion is added.

4. The mechanism must account for the inverse relation between the ease of oxidation and the formation of deposits.

Y.K. Sharma and K.M. Agrawal (1992), [20] studied influence of methanol extraction on the stability of middle distillate fuels. These studies indicated that methanol extraction could be successfully used to improve the stability of distillate fuels as well as to separating chemical precursor component responsible for instability.

B.T.Brooks (1926), [21] studied discoloration and gum formation of cracked gasoline, concluded that color is formed by adding acid (HCl or SO₂ which becomes H₂SO₄, or sulfonic acids formed by oxidation of thiols or disulfides) to fuels containing organic peroxide. He reported that air alone did not cause color, since pure hydrocarbon could be oxidized sufficiently to form gum but still had a light color. Similarly, only slight sample that were not permitted to contact air. The presence of both acid and air (required to form peroxides) was necessary. He noted that the organic peroxides, which are necessary for color formation, could be formed by the autoxidation of olefins, including some that are formed from cracking processes. He proposed that the organic peroxides have a

different role in color formation than gum formation. Organic peroxides induce polymerization of unsaturates to form gum.

B.H.Black, D.R.Hardy and E.J.Beal (1991), [22] noted that color can development from autoxidation reactions between the fuel and air. Hydroperoxide formation was orders of magnitude greater in bottles of jet fuel that were loosely covered compared to bottles that were tightly capped. This was a clear demonstration that oxygen from the air does react with the fuel.

G.W.Mushrush and J.G.Speight(1998),[23] concluded that acid–catalyzed condensation reactions are involved to a significant extent. These observations can be generalized to suggest that

1. Oxidized compounds can condense with heteroatom compounds to form fuel soluble oligomers and
2. The fuel soluble oligomers combine with organic acids to form colored species.

I.Bergeron,J.P.Charland and M.Ternan(1999), [24] studied color degradation of hydrocracked diesel fuel suggested that the final color forms in hydrocracked diesel fractions could attribute to the amount of two separate types of color precursors. One type is the unsaturated compound which was correlated with its density, since density can be an indication of aromatic content and other type is the compounds containing heteroatoms which was correlated with the sulfur and nitrogen contents of diesel fraction.

From several research above leading to the investigation of impact of antioxidants on the stability of diesel fuel oil under different oxidizing conditions

by modify the standard method for evaluation of thermal and oxidative stability including color degradation. We also study of the effectiveness of antioxidant additives, suitable type of antioxidant additives and optimum dosage of use to improve stability of this fuel for preservation at long term period.



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CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Oxygen gas was a commercially available extra dry oxygen of not less than 99.6 % purity obtained from TIG Trading Limited.

3.1.2 n – Heptane, analytical grade was obtained from Merck.

3.1.3 Toluene, analytical grade was obtained from Fluka.

3.1.4 Acetone, reagent grade was obtained from Merck.

3.1.5 Methanol, analytical grade was obtained from BDH.

3.1.6 Isooctane 99.75 % purity or better and containing no more than 0.10 % n–heptane was obtained from Merck.

3.1.7 Acetic acid solution:

Mixed 4 ml of concentrated hydrochloric acid (HCl, SP.GR. 1.19) with 996 ml of glacial acetic acid (CH₃COOH).

3.1.8 Potassium dichromate solution standard (0.1 N)

Dissolved 2.452 g of the purified K₂Cr₂O₇ in water and dilute to 500 ml in volumetric flask.

3.1.9 Potassium dichromate solution, standard (0.01 N)

Dilute 100 ml of 0.1 N K₂Cr₂O₇ solution with water to 1000 ml in a volumetric flask.

3.1.10 Potassium iodide solution

Dissolve 120 g of potassium iodide (KI) in 100ml of water

3.1.11 Sodium thiosulfate solution, standard (0.1 N)

Dissolved 12.5 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) plus 0.1 of sodium carbonate (Na_2CO_3) in 500 ml of water.

3.1.12 Sodium thiosulfate solution, standard (0.005 N)

Diluted 100 ml of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution with water to 2000 ml in volumetric flask.

3.1.13 Starch solution

Prepared soluble starch solution by dissolving 1 g of soluble starch plus a few milligrams of mercuric iodide (HgI_2) in 100 ml of boiling water.

3.1.14 1,1,2-Trichloro-1, 2, 2-trifluoroethane was obtained from Merck.

3.2 Fuel samples

The fuel samples were heavy gas oil (HGO) and light gas oil (LGO) from straight - run atmospheric distillate processing. Hydrocracked Gas Oil (HCGO) was a crack from hydrocracking processing. Blends of each fraction (HGO, LGO and HCGO) into the finished form of diesel fuel (or automotive gas oil; ADO) without blended any additives and high speed diesel which was added with some additives to improve fuel stability, were obtained from Alliance Refinery Company (ARC). Their physical and distillation characteristics are given in tables 3-1 and 3-2, respectively.

Table 3-1 Physical properties of fuel samples

Sample Nature	Test Method	HGO					LGO					HCGO					Blends of HGO ,LGO and HCGO into HSD					HSD with Unknown Additive
		A	B	C	D	E	F	G	H	I	A	B	C	D	E	F	G	H	I			
Aromatic Content, % vol	IP 391	25.59	24.86	28.10	18.38	23.23	24.97	25.51	25.78	24.98	1.78	1.82	1.13	1.34	1.50	1.27	1.30	1.33	1.22			
N Heteroatom Content,% vol	ASTM D 5291	0.8418	0.8413	0.8423	0.8410	0.8413	0.8423	0.8428	0.8433	0.8379	36.5	36.4	38.4	38.7	36.2	36.4	36.5	36.3	37.3			
Density at 15 ° C (g/cm ³)	ASTM D 1298	3.969	2.390	3.980	3.348	3.975	3.916	3.834	3.936	2.974	0.129	0.035	0.022	0.045	0.054	0.051	0.046	0.035	0.029			
API Gravity @ 60/60 ° F	ASTM D 445	0.25	0	0	0.25	0.25	0.25	0.25	0.25	0.50	0.004	0.001	0.002	0.003	0.003	0.003	0.003	0.003	0.008			
Kinematic Viscosity @ 40 ° C ,mm ² /s (cSt)	ASTM D 4294	160	80	80	80	132	120	130	112	98	ASTM D 1500	ASTM D 4870	ASTM D 4530	ASTM D 2274 (Modified)	ASTM D 3703 (Modified)	ASTM D 525 (Modified)	ASTM D 93	ASTM D 2709				
Sulfur content , % wt		2.57	1.57	1.83	1.35	2.01	1.49	1.66	1.91	0.66	0.004	0.001	0.002	0.003	0.003	0.003	0.003	0.003	0.005			
ASTM Color		8.18	4.10	3.33	5.30	7.41	4.48	4.20	5.58	7.45	0.01	traces	traces	traces	traces	traces	traces	traces	0.005			
Total Sediment, %wt		99	64	81	67	95	91	89	91	69	0.01	traces	traces	traces	traces	traces	traces	traces	0.005			
Micro carbon residue , mg/kg		0.01	traces	traces	traces	0.005	0.005	0.005	0.0025	0.005	0.01	traces	traces	traces	traces	traces	traces	traces	0.005			
Total Insoluble , mg/100 ml																						
Peroxide value (PV),mg/kg																						
Induction Period at 95 ° C, h																						
Flash Point, ° C																						
Water and Sediment Content , % vol																						

Table 3-2 The distillation analyses (°C) of the fuel samples (by ASTM D 86)

Sample	A	B	C	D	E	F	G	H	I
IBP	220.0	171.6	204.7	220.6	217.4	218.6	216.0	218.3	179.6
5	236.9	196.6	226.5	235.2	236.8	238.7	235.0	237.0	199.8
10	245.0	204.0	235.3	242.7	244.6	246.6	243.0	244.8	208.6
20	260.3	216.5	246.5	255.3	256.0	258.4	254.1	256.2	227.8
30	273.0	227.3	256.4	267.5	266.8	268.9	264.9	266.9	245.8
40	286.1	238.9	267.0	280.1	277.6	279.5	276.0	277.4	262.1
50	299.2	249.2	279.8	292.2	289.1	291.2	287.4	289.1	277.6
60	312.2	259.7	294.9	305.3	301.4	303.8	300.0	301.5	292.5
70	327.1	271.5	313.0	319.8	315.9	318.7	314.4	316.2	308.7
80	344.0	285.6	334.3	337.0	333.5	335.9	332.1	333.8	327.2
90	367.3	306.1	359.4	360.1	356.3	358.4	355.6	356.8	349.7
95	386.7	324.8	375.4	378.8	373.1	374.6	372.9	373.7	364.8
FBP	390.4	340.2	382.2	389.1	308.9	380.6	380.2	380.8	373.7

where :

A = Heavy gas oil (Straight-run distillate).

B = Light gas oil (Straight-run distillate).

C = Hydrocracking gas oil.

D-H = High speed diesel (or Automotive diesel oil; ADO) without any additives and was varied the ratio of HGO : LGO : HCGO are given in table 3-3.

I = High speed diesel which added unknown additive.

Table 3-3 Ratio of blends of diesel fuels (or automotive diesel oil; ADO)

Sample	% of Distillate Fraction		
	HGO	LGO	HCGO
D	65	10	25
E	70	10	20
F	65	5	30
G	65	15	20
H	60	10	30

3.3 Antioxidant additives and others

The primary antioxidants used were obtained from the Lubrizol Corporation, Pennzoil and U.C Marketing Co., Ltd. The proprietary lubricity additive was obtained from the Lubrizol Corporation. Some physical characteristic is given in table 4. The heavy gas oil (HGO) containing 0.129 % wt sulfur and 1.78 % wt nitrogen, were used as a source of natural fuel inhibitors (natural antioxidant).

Table 3-4 Physical characteristics of fuel additives

Physical Characteristics	Type of Additives					
	A	B	C	D	E	F
Specific Gravity at 15.6 °C (60°F)	0.9010	0.8644	0.9750	0.8970	0.9710	0.8740
Viscosity @ 40 °C , cSt	37.5	24.20	-	15.05	-	-
Viscosity @ 100 °C , cSt	-	-	271.7	4.08	119.0	1.353
Flash point , °C	-	72	-	-	-	-
Water Content , % vol	-	dry	-	-	-	-

The additives were used to study the impact on the stability of diesel fuel oil as the following :

3.3.1 Additive A

This additive is an alkylamine antioxidant type which composed of *N,N*-di-*sec*-butyl-*p*-phenylenediamine(45-55%),*N,N,N*-tri-*sec*-butyl-*p*-

phenylenediamine(0-1%),*N*-*sec*-butyl-*p*-phenylenediamine(0-1%),*p*-phenylenediamine(0-1%)and nitrogen (0.94 %) in a heavy aromatic naphtha (45-55 %).

3.3.2 Additive B

This additive is an alkylphenol antioxidant type, composed of 2,6-di-*tert*-butyl-*p*-cresol solute in light aromatic naphtha

3.3.3 Additive C

This additive is N, N'-disalicylidine-1,2-propanediamine. It is used as metal deactivator additive.

3.3.4 Additive D

This additive is a polymeric dispersant of the type polyalkylene succinimides, composed of alkenyl carboxylic acid (50– 59.9 %), 9,12–octanecadienoic acid (5 – 9.9 %), naphthalene (1.3 %), octadecanoic acid (0.5 – 1.5 %) and 1,2,4 –trimethylbenzene (0.1–0.9 %) in a heavy aromatic naphtha (10 – 19.9 %). It is a dual function additive, which acts as a dispersant and a lubricity additive.

3.3.5 Additive E

This additive is a blend of additive A with additive B in ratio of 1:1. It is used as a combined additive.

3.3.6 Additive F

This additive is a blend of additive A with additive D in ratio of 1:1. It is used as a combined additive.

3.4 Instruments and apparatuses

3.4.1 FT-IR Spectrophotometer

The FT – IR Spectrophotometer model 2000 series (Double Beam) from Perkin Elmer was used for Characterization at working range of 400 – 4000 cm^{-1} .

3.4.2 ASTM Color Scale Tester

The ASTM Color Scale Tester model AC-1 from Yoshida was used to determine the color by ASTM D 1500 standard test method.

3.4.3 CHNS/O Analyzer

The CHNS /O Analyzer Model PE 2400 series II from Perkin Elmer was used to determine the elements such as nitrogen , sulfur carbon and hydrogen.

3.4.4 Centrifugal for BS & W Analyzer

The Centrifugal for BS & W Analyzer Model H – 215 from Kokusan was used to determine water and sediment content in diesel Fuel Oil in accordance with ASTM D 2709 standard test method.

3.4.5 API Hydrometer

The API Hydrometer model ASTM (E 100) 4H from Precission was used to determine API Gravity at 60 °F and corrected to density @ 15 °C in accordance with ASTM D 1298 standard test method.

3.4.6 Kinematic Viscosity Apparatus

The Kinematic Viscosity Bath model VB-M6P from Yoshida and Transparent Glass Viscometer type model size no.75 were used to determine

kinematic viscosity at 40 °C in accordance with ASTM D 445 standard test method.

3.4.7 Automatic Flash Point Tester (PMCC)

The Automatic Flash Point Tester (PMCC) model MP 329 from Herzog was used to determine flash point of fuel samples in accordance with ASTM D 93 standard test method.

3.4.8 Micro Carbon Residue Tester

The Micro Carbon Residue Tester from Alcor was used to determine carbon residue (micro) of fuel sample before aging at each tested condition in accordance with ASTM D 4530 standard test method.

3.4.9 Automatic Distillation Machine

The Automatic Distillation Machine model MP 627 / 628 from Herzog was used to determine distillation characteristics of fuel samples in accordance with ASTM D 86 standard test method.

3.4.10 Total Sediment Tester

The Total Sediment Tester from seta was used to determine total insoluble in n – heptane (deposit and sediment formation) before and after aging at each tested condition by the modified ASTM D 2274 standard test method.

3.4.11 Sulfur Analyzer

The Sulfur Analyzer model LAB X-3000 from Oxford was used to determine sulfur content of fuel samples in accordance with ASTM D 4294 standard test method.

3.4.12 Oxidation Stability Tester

The Oxidation Stability Tester model metallic oxidation bath from Analis was used to determine induction period of fuel samples by modified ASTM D 525 standard test method.

3.4.13 Iodine Number Flask

The Iodine Number Flask was used to determine peroxide value of fuel samples by modified ASTM D 3703 standard test method.

3.5 Experimental procedures

3.5.1 Determination of basic characteristics

Each fraction of distillate fuels and blend components which was added with additives (finished products for sale) and without any additives before, were tested for the basic characteristic by standard test method as the following :

3.5.1.1 Aromatic content was determined by IP 391 standard test method [25].

3.5.1.2 Nitrogen content was determined by ASTM D5291 standard test method [26].

3.5.1.3 Sulfur content was determined by ASTM D 4294 standard test method [27].

3.5.1.4 Density and API Gravity were determined by ASTM D 1298 standard test method [28].

3.5.1.5 Flash Point was determined by the Pensky Martens Closed Cup Tester (Automatic) in accordance with ASTM D 93 standard test method [29].

3.5.1.6 Kinematic Viscosity at 40°C was determined by ASTM D 445 standard test method [30].

3.5.1.7 Micro Carbon Residue was determined by ASTM D 4530 standard test method [31].

3.5.1.8 Water and Sediment Content was determined by ASTM D 2709 standard test method [32].

3.5.1.9 Distillation characteristics were determined boiling range of each diesel fraction to be tested where were following to ASTM D 86 standard test method by the automatic distillation machine [33].

3.5.2 Measurement of diesel fuel stability

For this study, we classified 2 types of fuel stability into oxidative stability and thermal stability. We have modified ASTM D2274 standard method to evaluate the thermal stability of diesel fuels and modified ASTM D 3703 and ASTM D525 standard methods to measure their oxidation stability of diesel fuels and modified ASTM D1500 standard method to evaluate the color development.

3.5.2.1 Determination of oxidation stability

Two approaches were used to determine oxidation stability.

3.5.2.1.1 Induction period [34].

The induction period method was used to determine oxidation stability before significant production of peroxides (or secondary products) began. The induction period was very dependent on the conditions of the oxidation experiment. The induction period of diesel fuel samples monitored by monitoring the consumption of oxygen. Summary of test method; the fuel sample was oxidized in a bomb initially filled at 15 to 25 °C with oxygen pressure at 690 kPa (100 psi) and heated at variable temperatures at 25, 45, 65, 85, 95 and 100°C, respectively. The pressure was read at intervals or recorded continuously until the break point was ready. The time required for the sample to reach this point was the observed induction period at the temperature of test.

a) Reagents and materials

1. Gum Solvent: mixture of equal volumes of toluene and acetone, both of which shall be of 99 % minimum purity.
2. Oxygen Gas: commercially- available extra dry oxygen of not less than 99.6 % purity.

b) Preparation of apparatus

1. Washed the glass sample container with gum solvent until free from gum. Rinsed thoroughly with water and

immersed the sample container and cover in detergent cleaning solution.

2. Removed container and cover from the cleaning solution by means of corrosion – resistant steel forcep and handle only with forcep thereafter. Washed thoroughly, first with tap water, then with distilled water, and dried in an oven at 100 to 150 °C for at least 1 h.
3. Drain any diesel oil from the bomb and wipe the inside of the bomb and lid, first with a clean dry cloth. Removed the filler rod from the stem and carefully clean any gum from the stem, rod and needle valve with gum solvent. The bomb, the valve and all connecting lines shall be thoroughly dry before each test is started.

c) Procedure

1. Bring the bomb and diesel fuel oil to be tested to a temperature of 15 to 25 °C. Placed the glass sample container in the bomb and added 50 ± 1 ml. of sample. Covered the sample container, closed the bomb, and using a quick release air coupling introduce oxygen until a pressure of 690 to 705 kPa (100 to 102 psi) was attained. Allow the gas in the bomb to escape slowly in

order to flush out the air originally present (Release the pressure at a slow uniform rate through the needle valve at a rate not exceed 350 kPa (50 psi) per min. Introduced oxygen again until a pressure of 690 to 705 kPa (100 to 102 psi) was attained and observed for leaks, ignoring an initial rapid drop in pressure [generally not over 41 kPa(6 psi)] which may be observed because of the solution of oxygen in sample. When the rate of pressure drop did not exceed 7 kPa (1 psi) in 10 min assume the absence of leaks and proceeded with the test without repressuring.

2. Placed the charged bomb in the vigorously bath which settled up to test temperature, being careful, to avoid shaking, and recorded the time of immersion as the starting time, maintained the temperature of the controlled bath until the breakpoint of sample tested has been reached. Observed the temperature to the nearest 0.1 °C at intervals during the test, and recorded the average temperature to the nearest 0.1 °C as the temperature of the test. Made a continuous record of pressures in the bomb by the oxidograph until reading a point by pressure drop exactly 14 kPa (2 psi) in 15 min

and succeeded by a drop of not less than 14 kPa (2 psi) in 15 min.

3. Recorded the number of minutes from the time of the bomb was placed in the bath until the breakpoint has been reached as the observed induction period at the temperature of the test.

3.5.2.1.2 Peroxide value [35]

The peroxide value (PV) was determined by modified ASTM D 3703 standard test method. A measurement of peroxide number (peroxide value, PV) can be used as an index of current oxidation status only if the peroxides formed are stable enough so that they do not decompose after formation. The magnitude of the peroxide number is an indication of quantity of oxidizing constituents present. Deterioration of diesel fuel oil results in the formation of peroxides and other oxygen-carrying compounds. The peroxide number measures those compounds that will oxidize potassium iodide.

a) Procedure

The procedure to determine peroxide value was a modified ASTM D 3703 where details of test procedure are following below:

1. Selected the appropriate weight of sample from the following table

Estimated peroxide number, mg/kg	Sample weight, g
0 to 10	50
11 to 30	35
31 to 50	25
51 to 80	10
81 to 100	5

2. Weighed the sample into a 250 ml iodine flask that has been flushed with nitrogen. Added 25 ml of 1,1,2-trichloro-1, 2, 2 -trifluoroethane. Passed a vigorous flow of nitrogen or carbon dioxide through the solvent for 1 min, then, without stopping the gas flow, added 20 ml of acetic acid solution and reduced the flow of gas so that the rate is one bubble per second, added 2 ml of KI solution and swirl rigorously for exactly 30s. Setted the flask aside to stand for $5 \text{ min} \pm 3\text{s}$.
3. At the end of reaction period, added 100 ml of water and stop the gas flow. Titrated with 0.005 N $\text{Na}_2\text{S}_2\text{O}_3$ solution to a light yellow color. Added 5 ml of starch solution and continue the titration to the disappearance of the blue color.

4. Titrated reagent blanks immediately before and after each set of unknown determinations, following the same procedure as for the sample.

b) Calculation :

1. Calculate the peroxide number as follows :

$$\text{Peroxide Value, mg/kg} = [(A - B) N \times 1000 \times 8] / S$$

Where

A = millilitres of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for titration of the sample,

B = millilitres of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for titration of the blank,

N = normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution, and

S = grams of sample used

3.5.2.2 Determination of thermal stability [5]

The ASTM D 2274 standard test method was used to determine the total insoluble (deposit and sediment formation) which indicated to the thermal stability of diesel fuel oil before and after oxidation of the sample at each tested temperature (25, 45, 65, 85, 95 and 100 °C) for 24 hrs in oxidation bomb with oxygen pressure of 690 kPa(100 psi). After cooling for about 2 h, the sample was filtered on a previously weighed 0.8 μm cellulose nitrate filter paper. The insoluble sediment was determined gravimetrically and the adherent gum was recovered from glass sample container (oxidation cell) with a trisolvant (TAM ; a

solution of equal volumes of toluene, acetone, and methanol. The weights of sediment and adherent gum were totalled as insoluble gum. The total of insoluble deposits is reported as mg / 100 ml.

3.5.2.3 Determination of color development [36]

The color development is the parameter which can be used to indicate the oxidation and thermal stability of fuel. The color of the fuel sample before and after aging in oxidation cell can be determined by ASTM D 1500 standard test method. A sample is placed in a container and, using a standard light source, is compared with colored glass discs ranging in value from 0 (colorless) to 8.0 (dark red), in Steps of 0.5. The number of the matching glass or the higher of the two numbers where there is no exact match, is reported as the ASTM color. In accordance with ASTM D 1500, when an exact match cannot be found, the next higher ASTM color value is to be used, preceded by the letter L.

For the purpose of this study, the letter L was interpreted as being one – half an increment (0.25) lower than the color value chosen. For instance, a color value of 3.75 would be assigned to an ASTM color of L 4.0.

3.5.3 Study of N, S –heteroatom effects on diesel fuel stability

3.5.3.1 Sulfur -heteroatom containing effects

Prepared 0.030, 0.050, 0.075 and 0.100 % sulfur, by mass, of hydrocracking gas oil (HCGO) by spiked with thiophene (C_4H_4S); analytical grade into the sample to make concentrations of 0.030, 0.050, 0.075 and 0.100%, by mass, respectively, and the amount was determined according to ASTM D 4294 (X-ray fluorescence Technique). The 50 ± 1 ml of each prepared sample was taken to determine stability of fuel sample using the same procedure as in 3.5.2.1, 3.5.2.2 and 3.5.2.3.

3.5.3.2 N–heteroatom containing effect

Pipetted 0.03, 0.05, 0.075, 0.10 and 0.20 ml of pyridine (C_5H_5N); analytical grade and put into each 100 ml volumetric flask and added hydrocracking gas oil sample which was determined the nitrogen content by CHNS/O Analyzer according to ASTM D 5291. The volume was made up until 100 ml mark. The 50 ± 1 ml of each prepared sample that had different nitrogen content was taken into the oxidation cell and oxidized with oxygen pressure of 690 kPa (100 psi) at 25, 45, 65, 85, 95 and 100 °C until the breakpoint has been reached. The sample was tested for fuel stability by the following items below:

- a) Induction period at each tested temperature.
- b) Peroxide value after oxidation at each tested condition.
- c) Total insoluble (deposit or sediment formation) after oxidation at each tested condition.

d) ASTM Color after oxidation at each tested condition.

3.5.4 Study of the effects of aromatic content on the stability of diesel fuel

Unsaturated compound in diesel fuel is one type of color precursors which was correlated with its density, since density can be an indication of aromatic content, so for this study we used diesel fraction which have different density to evaluate stability of the fuel samples.

The procedure to study the stability of fuel sample during and after oxidized with oxygen was the same procedure as in 3.5.3.2 . The fuel sample used in this case were heavy gas oil, light gas oil, hydrocracking gas oil and diesel fuel (or automotive diesel oil) without additive as shown in table 3-1.

3.5.5 Study of the effects of component distribution on the stability of diesel Fuel

The diesel fuel samples used in this study were varied in the ratio of heavy gas oil per light gas oil per hydrocracking gas oil which were given in table 3- 3. The samples were tested of the stability during and after oxidized by the same procedure as in 3.5.3.2.

3.5.6 The impact of antioxidant additives on the stability of diesel fuel (varying in various conditions)

In this experiment, the fuel samples as shown in table 3-1 were blended with different types of antioxidant additives to study the impact of different types of antioxidant additives on the stability of diesel fuel. The prepared samples were varied in the oxidizing temperature, concentration of antioxidant additive, N, S-heteroatom content and the component distribution and its density. All of samples were oxidized in oxidation bomb at various test conditions same the procedures above. The summary of test conditions as shown in the following procedures below:

3.5.6.1 Varying in the oxidizing temperatures

Added 20 mg of each antioxidant additive into 1 L of sample D (which the sample was the blends of heavy gas oil, light gas oil and hydrocracked gas oil in the ratio of 65 : 10 : 25) and oxidized each prepared sample with oxygen pressure of 690 kPa (100 psi) in the oxidation bomb which the temperature was controlled at 25, 45, 65, 85,95 and 100 °C, respectively. Recorded the number of minutes from the time when the oxidation bomb was placed in the controlled bath until the breakpoint has been reached as the induction period at each tested temperature of each sample. The procedure to determine both oxidation and thermal stability of tested sample and color development were the same as in 3.5.2

3.5.6.2 Varying in the concentrations of each antioxidant additive

Added 20, 40, 60, 80, 100 and 120 mg of each antioxidant additive into 1 litre of each sample D to prepare the concentrations of each antioxidant additive in the samples as 20, 40, 60, 80, 100 and 120 mg/l, respectively. Then, each prepared sample was oxidized with oxygen pressure of 690 kPa (100 psi) at 95 °C in the oxidation bomb by the same procedure as in 3.5.2.1.2. The number of minutes was recorded from the time when the oxidation bomb was placed in the controlled bath at 95 °C until the breakpoint has been reached as the induction period at 95 °C, then followed by the procedure as shown in 3.5.2.1.2, 3.5.2.2 and 3.5.2.3, respectively.

3.5.6.3 Varying in the concentration of N, S-heteroatom

The samples A, B and C contained different amount of sulfur and nitrogen. Each antioxidant additive at 20 mg was added into 1 L of sample A, B and C, respectively and then oxidized the prepared samples with oxygen pressure of 690 kPa (100 psi) in oxidation bomb at 95 °C until the breakpoint has been reached, The number of minutes was recorded from the time when the oxidation bomb was placed in the bath until the breakpoint has been reached as the induction period at 95 °C, then followed by the procedures as shown in 3.5.2.1.1, 3.5.2.2 and 3.5.2.3, respectively.

3.5.6.4 Varying in the component distribution and its density

The samples D, E, F, G and H which different in the component distribution and density different was added with 20 mg of each antioxidant additive into 1 L of each prepared sample and then oxidized with oxygen pressure of 690 kPa (100 psi) at 95 °C in the oxidation bomb until the breakpoint was reached. The number of minutes was recorded from the time when the oxidation bomb was placed in the bath until the breakpoint has been reached as the induction period at 95 °C, then followed by the procedures as shown in 3.5.2.1.1, 3.5.2.2 and 3.5.2.3, respectively.

3.5.6.5 Varying in the reaction time

Sample D was selected as a representative of finished diesel for sale. It was blended with each antioxidant type and then oxidized at various temperatures. The reaction times were varied by the same procedure as shown in 3.5.2.1.1 and the total insoluble that occurred was determined with the same procedure as shown in 3.5.2.2 in order to evaluate the impact of antioxidants on the occurring of insoluble material at each reaction time. The result was compared to sample I which was a finished diesel fuel as same as sample D but it already contains unknown antioxidant. The summaries of tested conditions for investigation of the effects of reaction times on the efficiency of antioxidants are shown in table 3-5.

Table 3-5 Summaries of the test conditions for determination of the total insoluble.

Sample	Reaction time ,(h)	Test Temperature (°C)	Concentration of each Antioxidant Additive (mg/L)					
			A	B	C	D	E	F
D	0,6,12 , 24 , 48	25 , 45 , 65 , 85 , 95 , 100	0 , 20 , 40 , 60 , 80 , 100 , 120	0 , 20 , 40 , 60 , 80 , 100 , 120	0 , 20 , 40 , 60 , 80 , 100 , 120	0 , 20 , 40 , 60 , 80 , 100 , 120	0 , 20 , 40 , 60 , 80 , 100 , 120	0 , 20 , 40 , 60 , 80 , 100 , 120
I	0,6,12 , 24 , 48	25 , 45 , 65 , 85 , 95 , 100	0	0	0	0	0	0

3.5.7 Evaluation of antioxidants behavior on the stability of diesel fuel

The behavior of antioxidants from all impacts found on the stability of diesel fuel were investigated as in 3.5.6

3.5.8 Investigation of the optimum dosage of antioxidant additives

In this case, the same procedure as in the study of concentration effects which would be explained in 3.5.6.2 was used.

3.6. The impact of additive combination on the stability of diesel fuel.

100 mg of combination additives that prepared from mixed a dispersant with an antioxidant and metal deactivator in the ratio 1:1:1 was added into 1 litre of sample D. Then, the 50 ± 1 ml of each prepared sample was taken to oxidize with oxygen pressure of 690 kPa (100 psi) in oxidation bomb which temperature was controlled at 95 °C. The result was compared with single antioxidant additive and also compared to the straight run fuel (sample A) was selected as a representation of a source of natural antioxidant containing 0.129 % wt sulfur. All of the tested samples were investigated by the following procedure below:

- a) Induction period at each tested temperature.
- b) Peroxide value after oxidation at each tested condition.

- c) Total insoluble (deposit and sediment formation) after oxidation at each tested condition.
- d) ASTM Color after oxidation at each tested condition.

3.7 Further studies of the impacts of antioxidant additives to improve the stability of diesel fuel at the different storage conditions

The performance of antioxidant and other additive on improving of the diesel fuel stability was investigated by keep the sample at different storage conditions (setted in the dark, room temperature and outdoor) for one month, and the total insoluble and ASTM Color were determined by the same procedure as in 3.5.2.2 and 3.5.2.3, respectively. The samples were divided into 3 groups;

Group 1: the samples were kept in the dark to avoid light at ambient temperature.

Group 2: the samples were kept at in ambient temperature at room temperature (22 ± 3 °C).

Group 3: the samples were kept onsite were not protected from sunlight and uncontrolled ambient temperature.

All groups were comprise of samples A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P and Q which the component distribution were shown in table II. The stability of diesel fuels at different storage conditions before and after blended with antioxidant, dispersant and combination of these additives into samples A, C and D, respectively, were determined.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Basic characteristic determinations

The basic characteristics of diesel fuel samples used in the present study differed greatly in their physical properties and distillation characteristics which were tested by standard test method as shown in 3.5.1. The summaries of the properties of all fuel samples before oxidation at each tested condition are given in table 3-1 and 3-2, respectively.

4.2 Study of the stability of diesel fuel before introducing of antioxidant additives

Fuel stability is classified into 2 types as oxidation stability and thermal stability. The oxidation stability of diesel fuel is characterized by the induction period and peroxide value (PV). Moreover, the thermal stability is characterized by the total insoluble after oxidation. The stability also characterized by determined the color developed which is the parameter used to indicate the oxidation and thermal stability of fuels. For this research, the stability of diesel fuel is characterized in four parameters were as the indicator of stability. The results of the characteristic of fuel samples were shown below.

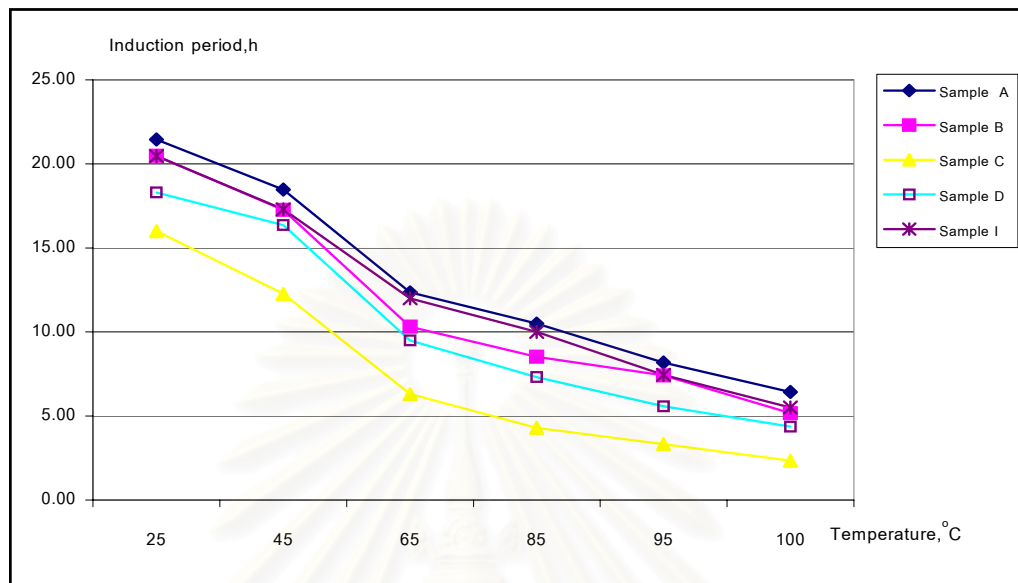


Figure 4-1 Induction period of diesel fuel before introducing of antioxidant additives after oxidation at various temperatures.

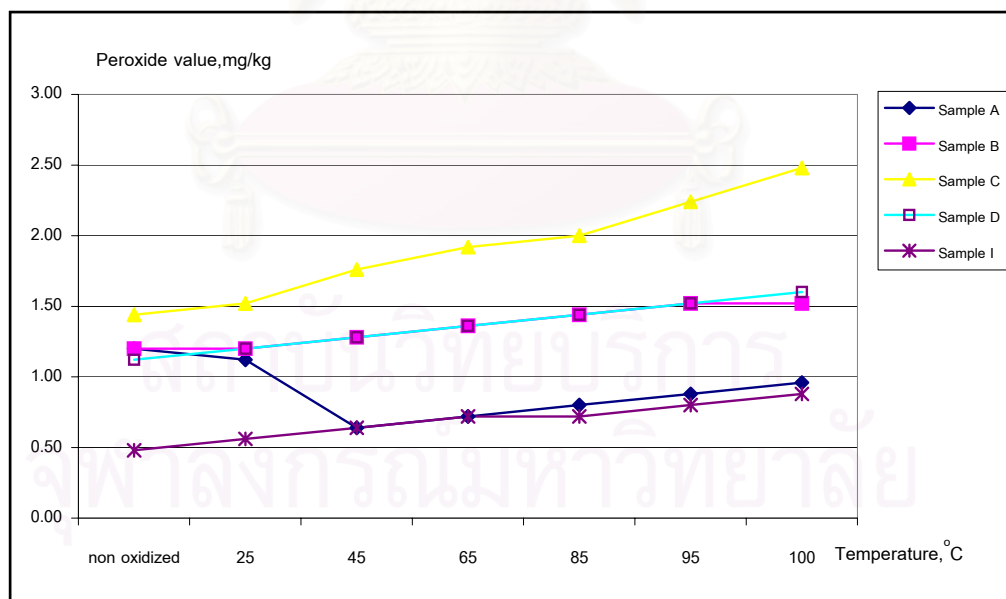


Figure 4-2 Peroxide value (PV) of diesel fuel before introducing of antioxidant additives after oxidation at various temperatures.

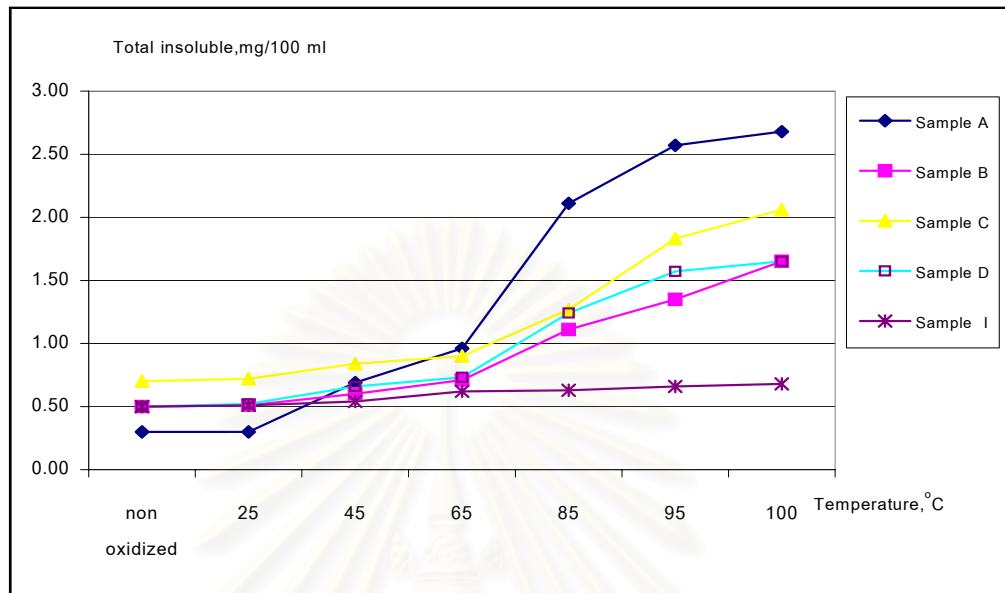


Figure 4-3 Total insoluble of diesel fuel before introducing of antioxidant additives after oxidation at various temperatures.

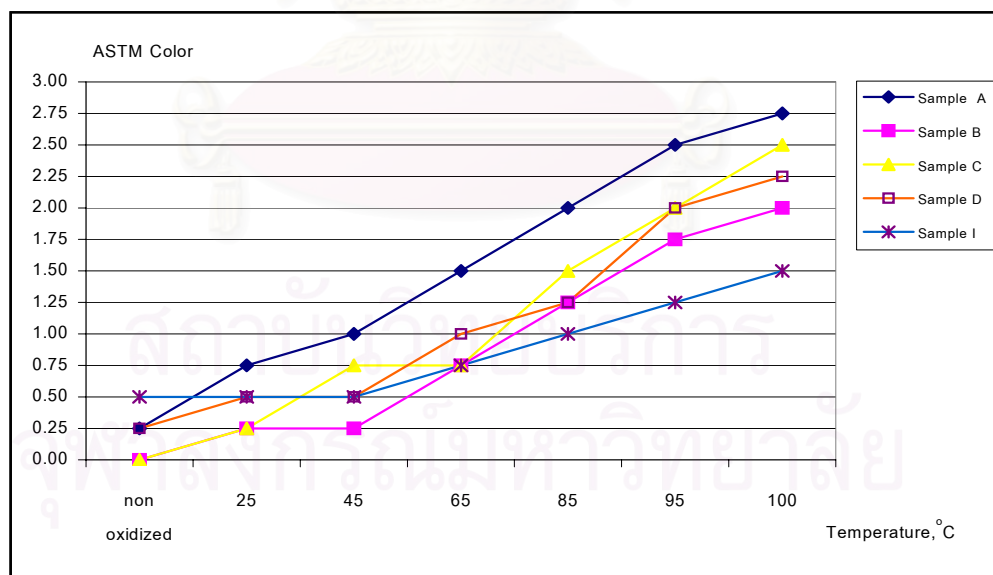


Figure 4-4 The ASTM Color of diesel fuel before introducing of antioxidant additives after oxidation at various temperatures.

In this section, the stability of distillate fraction which was a part of diesel fuel component in finished form and diesel fuel for sale before introducing any antioxidant additives was investigated. The stability was characterized by four parameters which were the induction period, the total insoluble, ASTM color and peroxide value (PV) that having well correlation for indication stability status after oxidized in oxidation bomb at various temperatures. The data were compared to diesel fuel finished form which blended with unknown additives (Sample I).

The results in the variation of temperatures of each diesel fuel sample from figures 4-1 to 4-4, indicated that the temperature was very dependent on the stability of all fuel samples. Figure 4-1, shows that the induction period of all samples decreased when the temperature was increased. It was readily apparent that sample A was more stable than sample I, because it gave the longest induction period. Data shows the stability in the order sample A > sample I > sample B > sample D > sample C.

From figure 4-2, the peroxide value (PV) of the tested samples before and after oxidation at each temperature was increased as the temperature increased. The high peroxide value was the indication that fuels had low stability or easy to be oxidized. The increase of PV, suggested that the stability was in the order of sample I ~ sample A > sample B > sample D > sample C.

Figure 4 -3 exhibited the total insoluble of diesel fuel samples under oxidizing conditions before introducing any additives into them. Our studies showed that the total insoluble was a linear dependence with the temperature. The results indicated that total insoluble was much greater in hydrocracking gas oil

(sample C) than in blends of with hydrocracking gas oil with straight-run distillate (Sample D), but sample A gave the highest total insoluble content and sample I gave the lowest insoluble content.

The results of temperature effects on color development of diesel fuel samples were shown in figure 4-4. The results indicated that much darker color developed in hydrocracking gas oil which had more aromatic content (28.10 %) than in the straight run distillate (or light gas oil; sample B). Sample A which having high sulfur and nitrogen content (0.129 and 1.78 % wt, respectively) gave the most dark color developed when the temperature was increased but sample I which as diesel fuel was blended with unknown additive gave the darkest color.

All of the results demonstrated that nitrogen and sulfur contained in the straight - run fuel distillates both heavy gas oil and light gas oil were significant influential on the stability of diesel fuel sample. They may act as an inhibitor or a natural antioxidant to slow oxidation of diesel fuels, so sample A, B and D were very effective in slowing oxidation (long induction period). This is consistent with previous observations concerning the presence of many natural antioxidants in straight run fuels make them more stability because natural antioxidants prevent the formation of ROOH or destroy some ROOH and reduce the rate of oxidation [39]. In contrast, the hydrocracking gas oil (sample C) that containing reduced levels of natural antioxidants and high aromatic content as a result of hydrotreatment was ineffective in slowing oxidation. Therefore fuels having reduced levels of natural antioxidant could have higher concentrations of ROOH (high PV) higher oxidation rates (short induction period) than the corresponding

straight-run diesel fuel. This indicated that the hydrocracking gas oil mainly controlled the tendency of diesel fuel sample towards instability.

The results also indicated that the total insoluble (deposit formation) which occurred from oxidation was dependent on sulfur, nitrogen and aromatic content in diesel fuel. Because the high concentration of them led to the formation of high deposit material by aromatic reaction with oxygen to produce peroxides and other oxidized intermediate material which were oxidation products. Then, these products reacted with sulfur and nitrogen containing compounds to form deposit material [16].

For color development of diesel fuel, the results at various temperatures indicated that much darker color was developed in the samples which had high levels of aromatic, sulfur and nitrogen content. The color development could support previous observation that the final color that formed in diesel fraction could be attributed to the amount of two separate types of color precursors. One type was the unsaturated compound and another type was the compound containing heteroatom [24].

The stability of sample D (diesel fuel which is finished form without any additives) was dependent on amount of the natural antioxidant, aromatic content and the component distribution. Sample I, was a diesel fuel finished form which was added already with unknown additive). The results indicated that the unknown additive in fuels had been postulated to play important roles in determining the oxidation behavior of blends of diesel fuel. It could be an antioxidant and other function to improve oxidation and thermal stability. It

improved by increasing the induction period, reducing total insoluble content and prevention from the formation of ROOH or by destroy some ROOH which can lead to very low ROOH concentrations. Moreover it could inhibit color development or reduce the rate of oxidation. These results suggested that diesel fuel needed some additives to improve the stability of diesel fuels.

4.3 Study of the effects of N,S-heteroatom on diesel fuel stability

4.3.1 Sulfur heteroatom containing effects

In this case, sample C which was hydrocracked gas oil is selected to study the effects of sulfur heteroatom containing on diesel fuel stability. Hydrocracking gas oil was representative of a large class of diesel fuels having reduced concentration of N, S-containing heteroatom species as a result of hydrotreatment. The thiophene (C_4H_4S) was added to hydrocracked gas oil to prepare the sulfur concentration of 0.030, 0.050, 0.075, 0.100, and 0.120, respectively. The effects of sulfur heteroatom containing on the stability of diesel fuel were shown in the figures below

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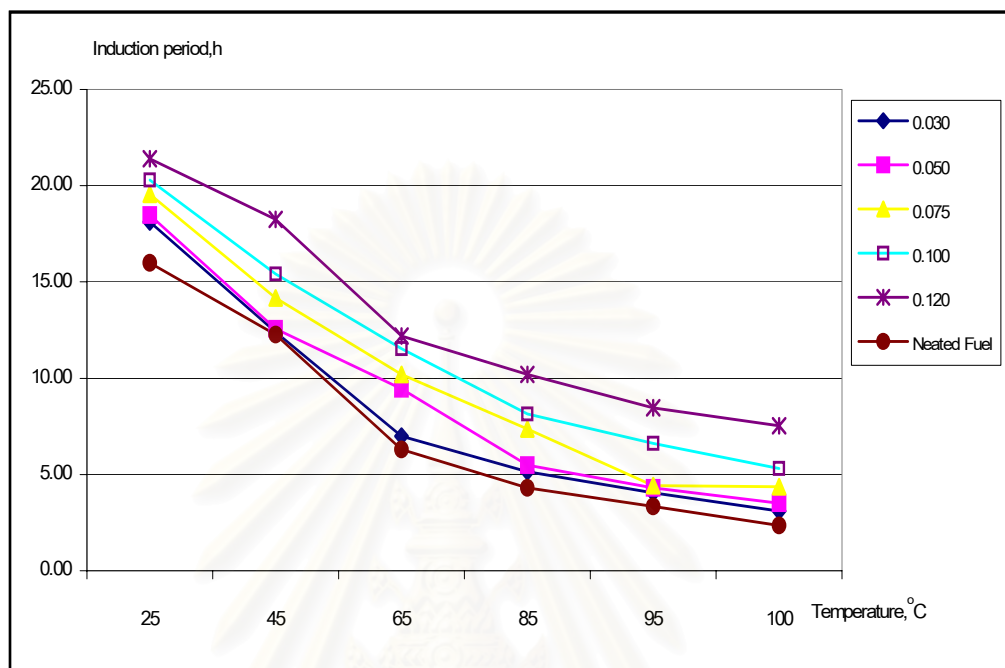


Figure 4-5 Induction period of hydrocracked gas oil after oxidation at various temperatures (varying in % of sulfur content)

For the induction period, the results showed that the sulfur content associated with the induction period of diesel fuel sample. The results indicated that the diesel fraction which having high concentration of sulfur increased the induction period. These data also confirmed that sulfur content had significant influence on the stability of diesel fuel. It could reduce the rate of oxidation (increase the induction period). However, the induction period depended upon temperature, and from the data above it was found that the induction period of all tested samples decreased when the temperature increased.

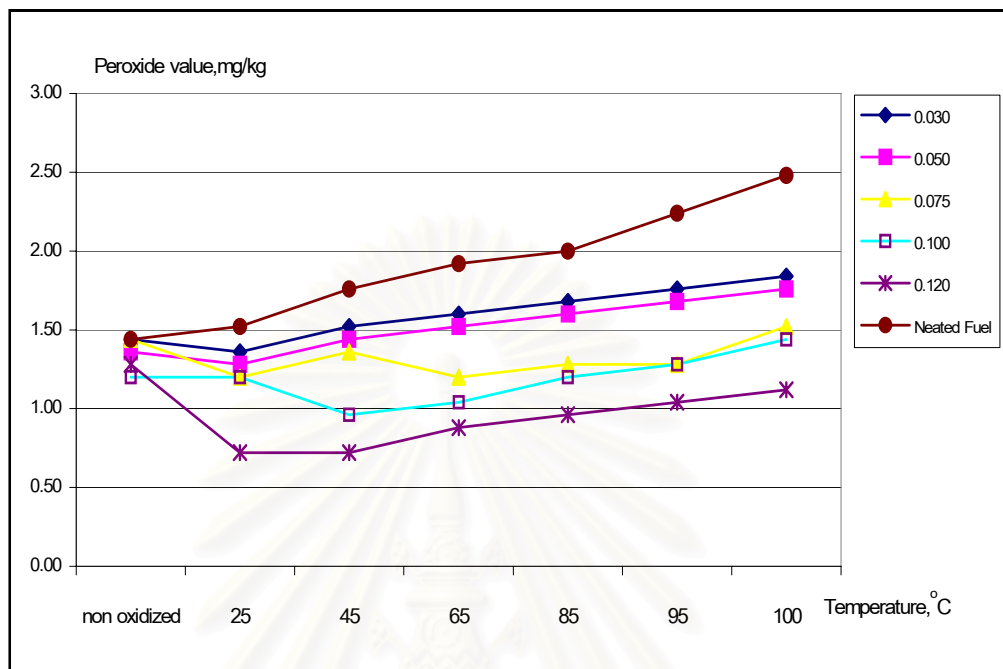


Figure 4-6 Peroxide value(PV) of hydrocracked gas oil after oxidation at various temperatures (varying in % of sulfur content)

The peroxide value (PV) of the tested sample after oxidation at the various temperature compared to non oxidized fuels, showed that neat fuel gave the highest peroxide value and the diesel fuel which had 0.120 % sulfur gave the lowest peroxide value. From these data, it indicated that sulfur was very effective in the peroxide value reducing or slow down the oxidation. It may prevent the formation of ROOH or destroy some ROOH induced to low ROOH concentration. The diesel fuel which low ROOH concentration could indicate more stability of fuel. Moreover, the results also indicated that the temperature was associated with the peroxide value and was contributed to the formation of ROOH species.

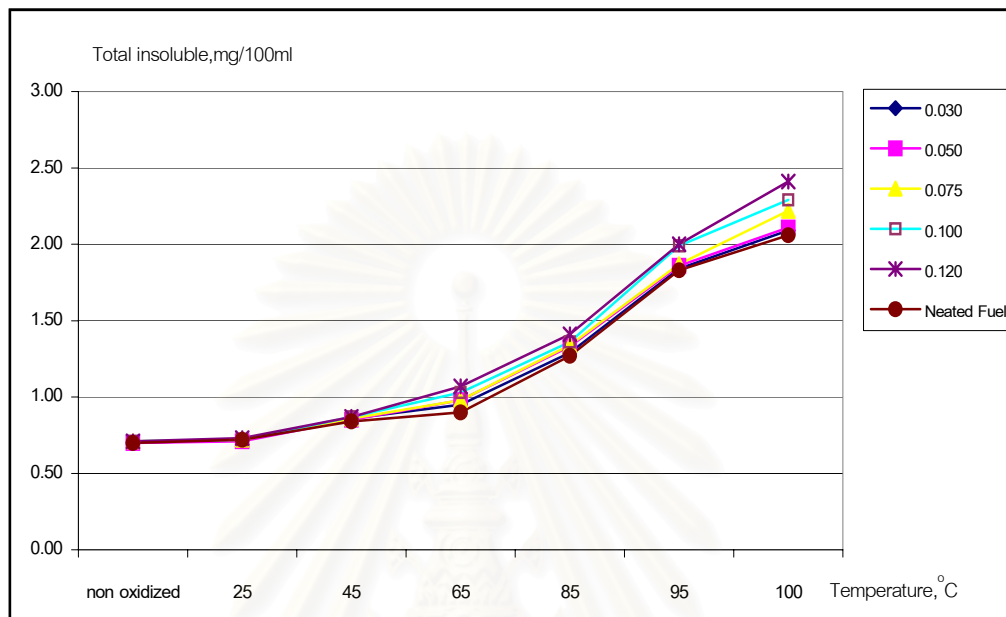


Figure 4-7 Total insoluble of hydrocracked gas oil after oxidation at various temperatures (varying in % of sulfur content)

For the total insoluble of the tested sample after oxidation at various temperatures as shown in figure 4-7 above, indicated that hydrocracking gas oil having 0.120 % sulfur gave the highest total insoluble, and the neat fuel gave the lowest total insoluble content. It was clear that sulfur content was very influential on total insoluble formation. At low temperature, the total insoluble formation was not differed from the non-oxidized fuels. These results showed that the temperature and sulfur content was significant influential on the total insoluble formation.

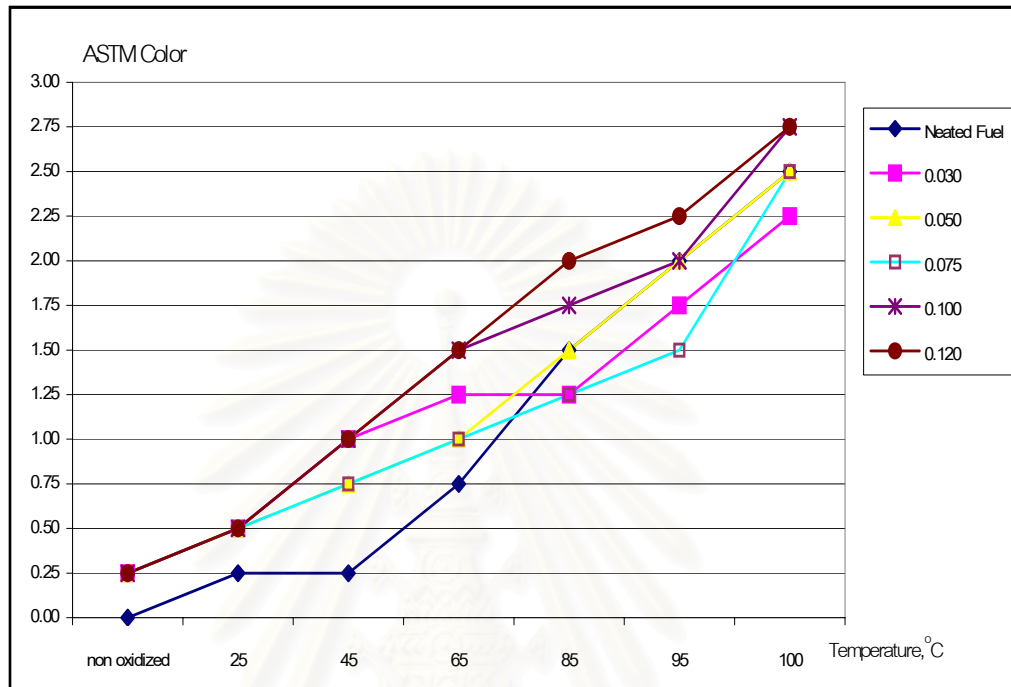


Figure 4-8 The ASTM Color of hydrocracked gas oil after oxidation at various temperatures (varying in % of sulfur content)

These data supported the observations that sulfur containing compound reacted with peroxides and other oxidized materials to form total insoluble (deposit materials) which could lead to overloading of filters and injector or nozzles plugging.

The effect of sulfur content on color development of diesel fuel was shown in figure 4–8. From above results, it indicated that sulfur content associated with color development. Generally, ASTM color allowance of the Ministry of Commerce (MOC) specification was 2.0 maximum, but in all diesel fractions the

color was increased from 0.25 to more than 2.0 after oxidation at 100°C. The results also showed that much darker color developed in the diesel fraction having high sulfur than the diesel fraction having low sulfur content. These data supported the hypothesis that sulfur was one type of color precursors which could condense with oxidation products to form colored species [24].

4.3.2. N-heteroatom containing effects

The effects of nitrogen heteroatom containing on the stability of diesel fuel are shown in the figures below.

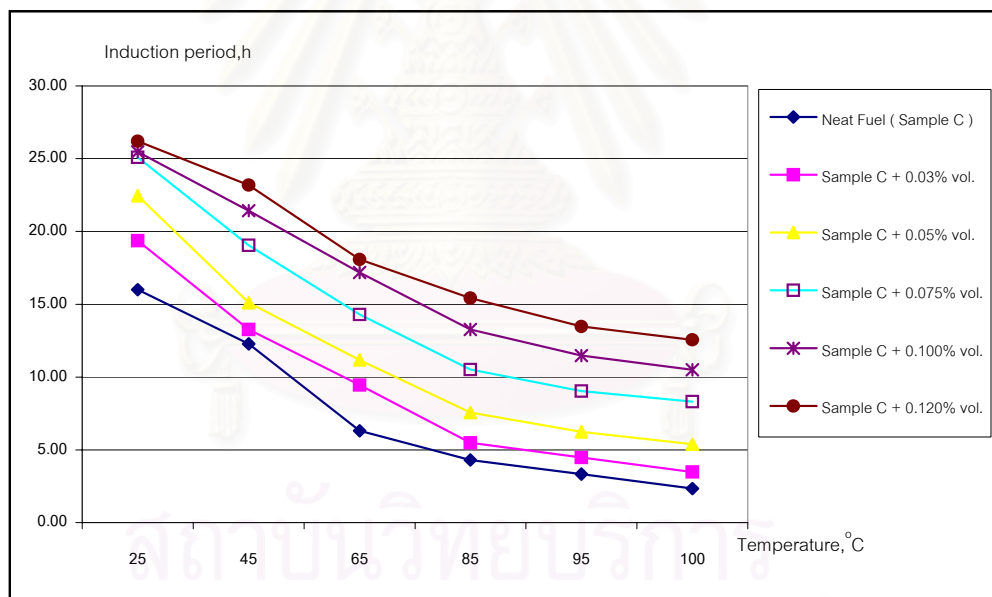


Figure 4-9 Induction period of hydrocracked gas oil after oxidation at various temperatures (varying in % of nitrogen content)

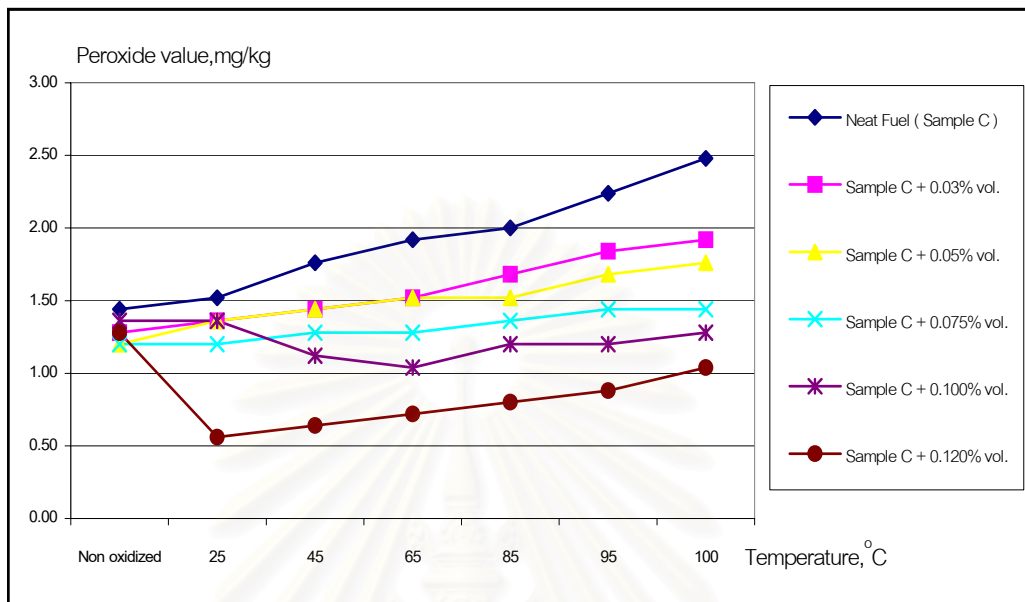


Figure 4-10 Peroxide value (PV) of hydrocracked gas oil after oxidation at various temperatures (varying in % of nitrogen content)

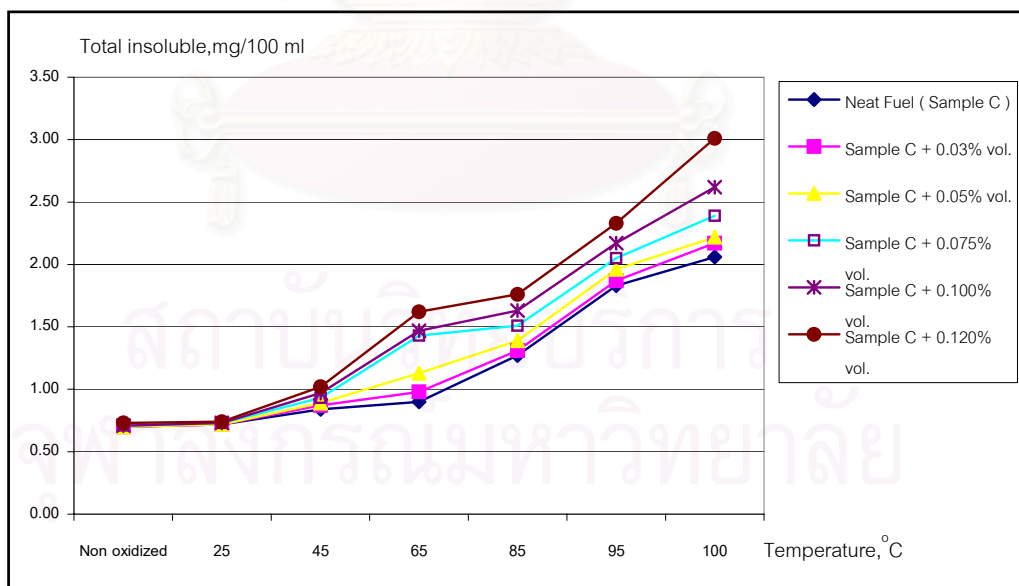


Figure 4-11 Total insoluble of hydrocracked gas oil after oxidation at various temperatures (varying in % of nitrogen content)

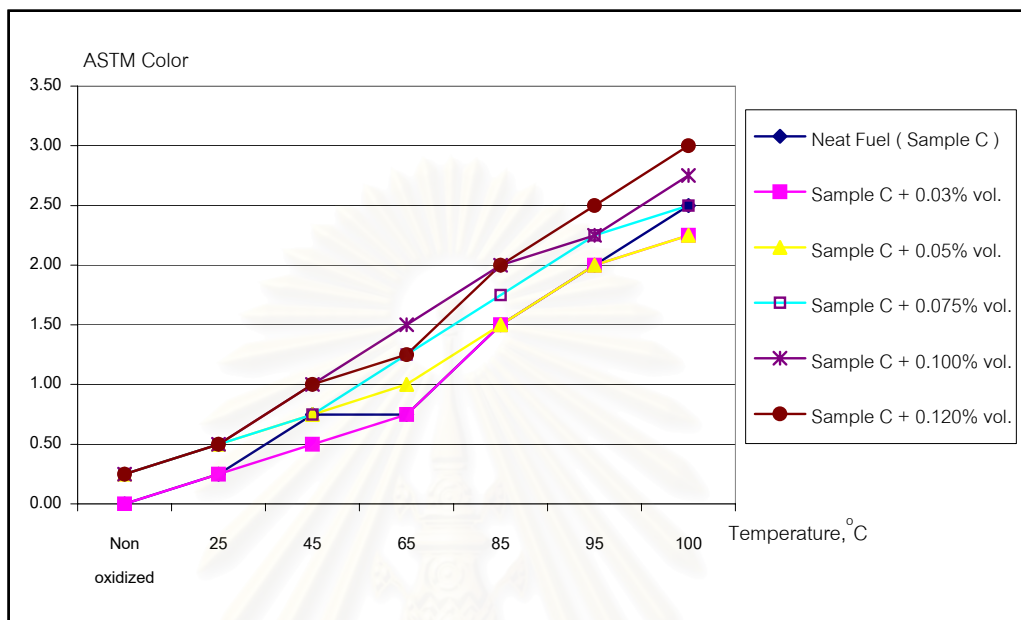


Figure 4-12 ASTM Color of hydrocracked gas oil after oxidation at various temperatures (varying in % of nitrogen content)

The effects of nitrogen content on the stability of diesel fuel were similar to these of sulfur. According to the results as shown in the figure 4–9 and figure 4–10, it indicated that the nitrogen containing compounds in diesel fuel samples could increase the induction period and reduce the peroxide value resulted in more stability by slow oxidation. However, the nitrogen effects on the diesel fuel concerned with the total soluble (deposit formation) and color developed as shown in figure 4–11 and figure 4–12, respectively. The results showed that the nitrogen compound could increase total insoluble which was the factor that led to overloading of filter and injector or nozzles plugging and also associated with the color development. The results indicated that hydrocracking gas oil (Sample C)

with 0.120 volume percent of pyridine gave the most color development and did not meet MOC specification. These data supported the hypothesis that nitrogen was one type of color precursors which could condense with oxidized products to form colored species [24]. Moreover the data above also supported the hypothesis that:

1. The nitrogen heteroatom should play an important role in the sediment formation of diesel fuel.
2. The ease of oxidation had inverse relationship to the formation of deposits (total insoluble increased) [18,23].

From the results in both 4.3.1 and 4.3.2, it demonstrated that sulfur and nitrogen heteroatom were significant influence on the stability of diesel fuel. All of the results showed that they could increase the induction period and may reduce or destroy peroxide species to low concentration that could be monitored by the reduction of peroxide value. However, at the high temperature all of the results indicated that the sulfur and nitrogen heteroatom mainly control the tendency of diesel fuel towards the formation of insoluble materials and much more color development. Moreover, sulfur and nitrogen compound could in condensed with peroxide and other oxidized products from autoxidation reaction to form colored species which were responsible for solid insoluble formation.

4.4. Study of the effect of aromatic content on the stability of diesel fuel

The effects of aromatic content on the stability of diesel fuel were evaluated. Eight diesel fuel samples with different in density were selected because the density could be an indication of aromatic content. The summary effects of aromatic content are shown in the figures 4-13 to 4-16 below.

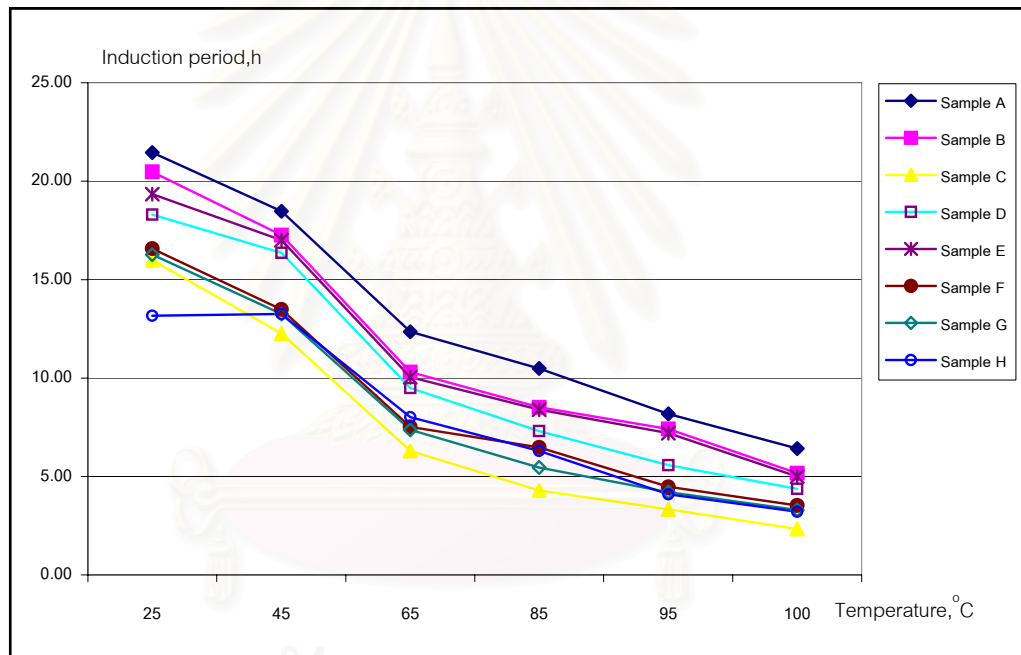


Figure 4-13 Induction period of diesel fuel after oxidation at various temperatures (varying in density)

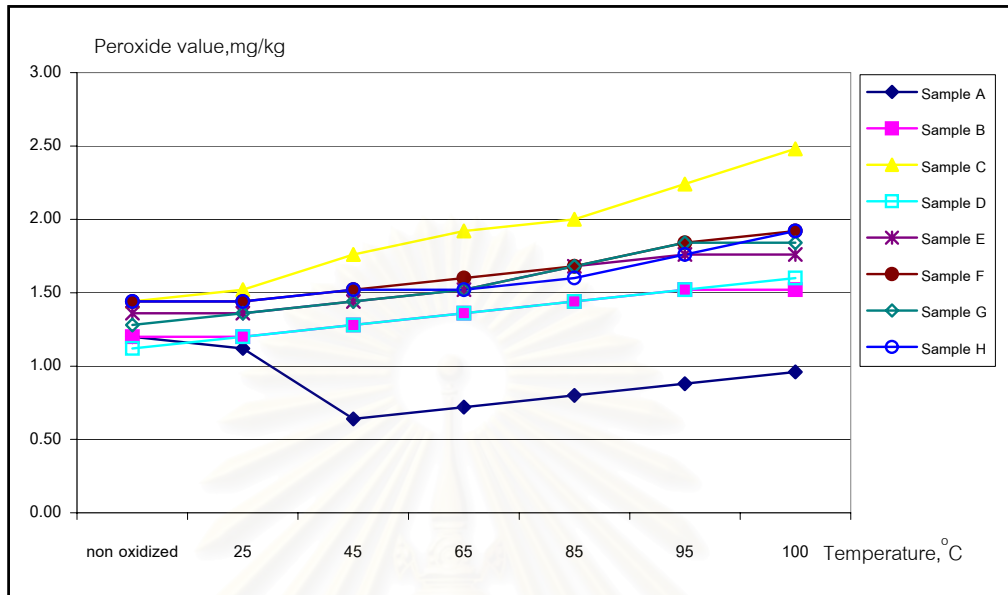


Figure 4-14 Peroxide value (PV) of diesel fuel after oxidation at various temperatures(varying in density)

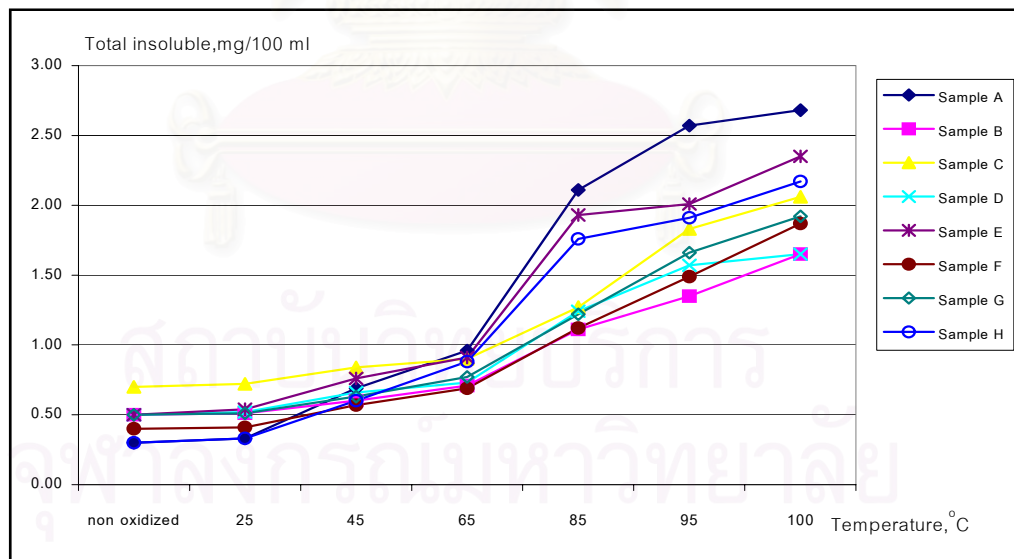
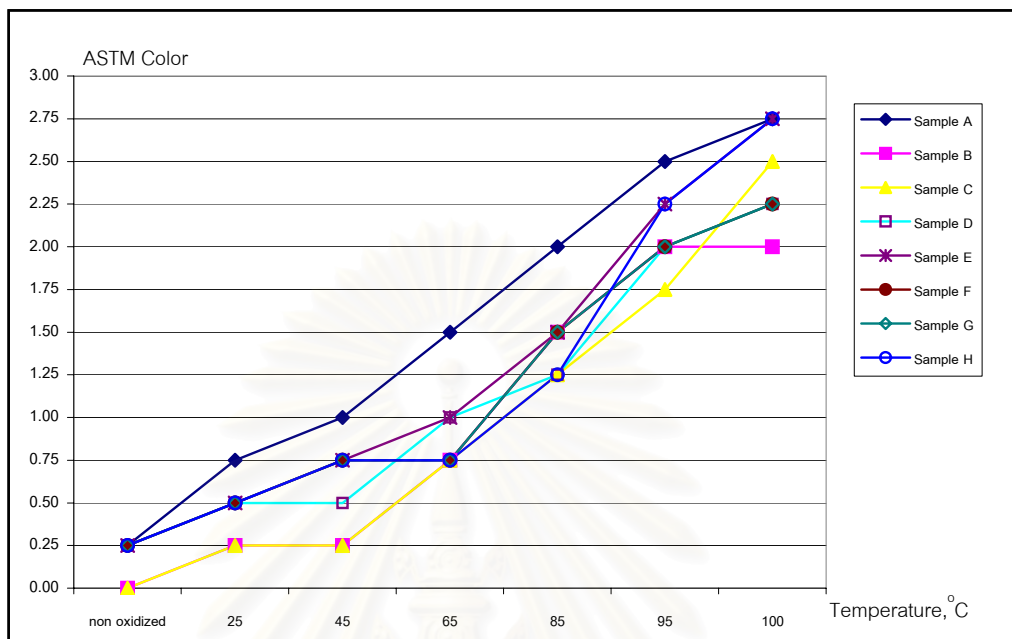


Figure 4-15 Total insoluble of diesel fuel after oxidation at the various temperatures(varying in density)



**Figure 4-16 ASTM Color of diesel fuel after oxidation at various temperatures
(varying in density)**

All of the results demonstrated that the aromatic compound had significant influence on the diesel fuel stability. The results in accordance with figure 4–13 showed that the fuel samples with high density gave shorter induction period than the samples with low density. For example, sample H with its density of 0.8433 gave shorter induction period than sample E with its density of 0.8413. However these results also correlated with peroxide value PV of fuel samples which were shown in figure 4–14. The results also indicated that the samples having high density should give higher peroxide value than the samples having low density.

These data demonstrated that aromatic content was ineffective in slowing the oxidation and effects on the stability of diesel fuels that it can decreased the

induction period and increased the peroxide value. Moreover, these results also indicated that sample A with high level of nitrogen, sulfur and aromatic content gave the highest stability when compared with other fuel samples. These data could be explained that the sulfur and nitrogen inhibited the oxidation predominantly.

However if we focus on the aromatic content effects especially, we found that aromatic compound contributed to fuel samples accelerate to form peroxide radicals induced to increase the rate of oxidation (longer induction period). The effects of aromatic compound well correlated with the formation of total insoluble and ASTM color of all samples after oxidation at each tested temperature. Aromatic compound effects concerned total insoluble and color developed which informed ASTM color as shown in figure 4-15 and figure 4-16, respectively. The results showed that aromatic compound existing in fuel sample was significant influence on increasing of the total insoluble formation and color development. For example, sample C with the highest aromatic content (28.10 % vol.) gave high total insoluble content (2.06 mg/100 ml) and color developed (ASTM color of 2.50). These data could support the hypothesis that aromatic compounds was one of color precursor as same as the nitrogen and sulfur heteroatoms. The results concluded that the aromatic compounds which contained in diesel fuel was the parameter that induced the fuels deterioration or contributed to formation of deposit material and to develop darker color.

4.5 Study of the effects of component distribution on the stability of diesel fuel.

The effects of component distribution on the stability of fuel samples were investigated by using blended of diesel fuel sample which different in the ratio of heavy gas oil per light gas oil and hydrocracked gas oil. The summary effects of component distribution are shown in figure 4-17 below.

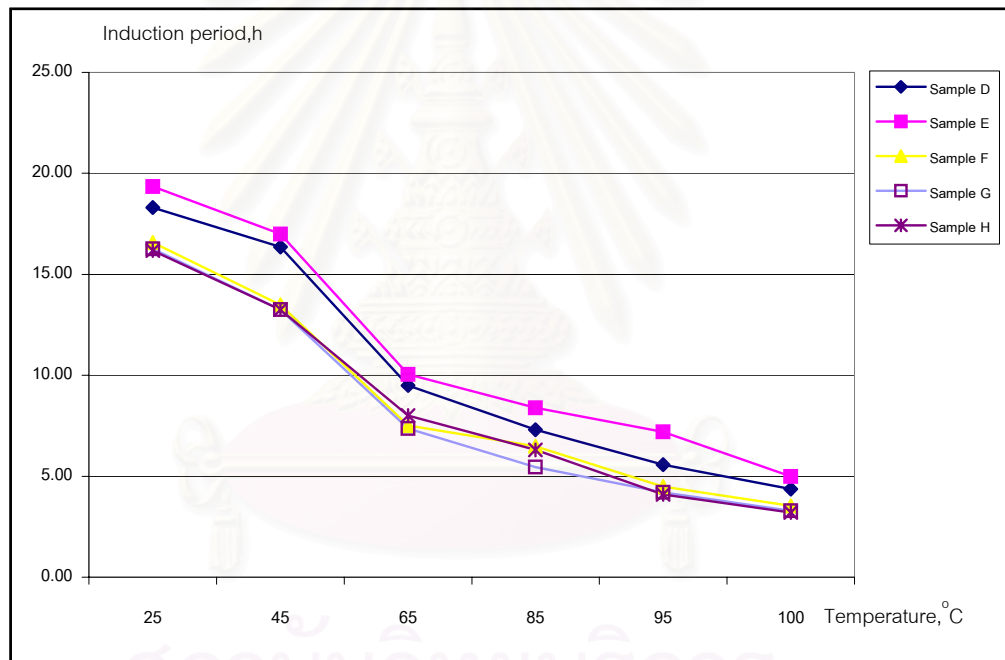


Figure 4-17 Induction period of diesel fuel after oxidation at various temperatures (varying in % component)

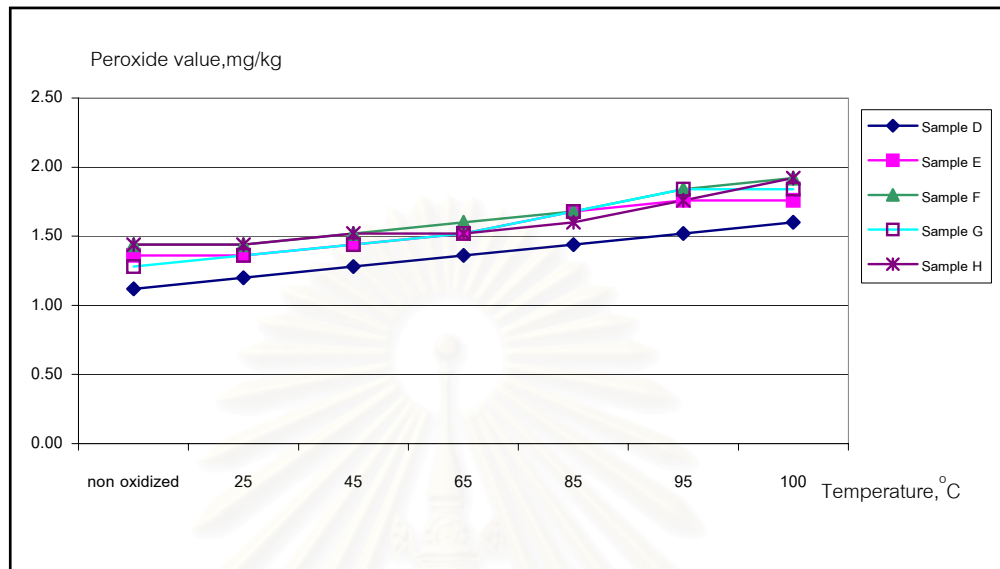


Figure 4-18 Peroxide value (PV) of diesel fuel after oxidation at various temperatures (varying in % component)

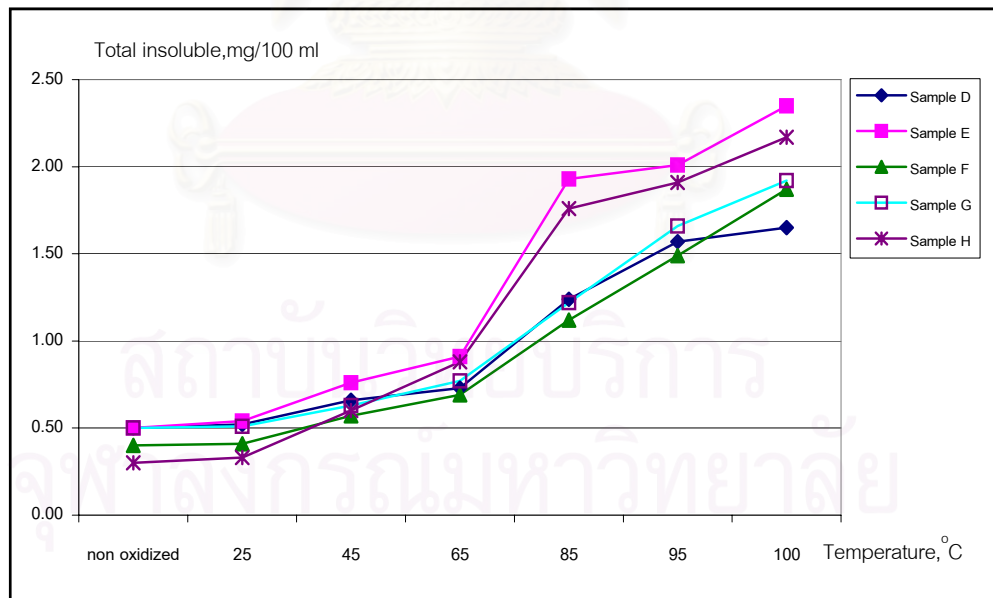


Figure 4-19 Total insoluble of diesel fuel after oxidation at various temperatures (varying in % component)

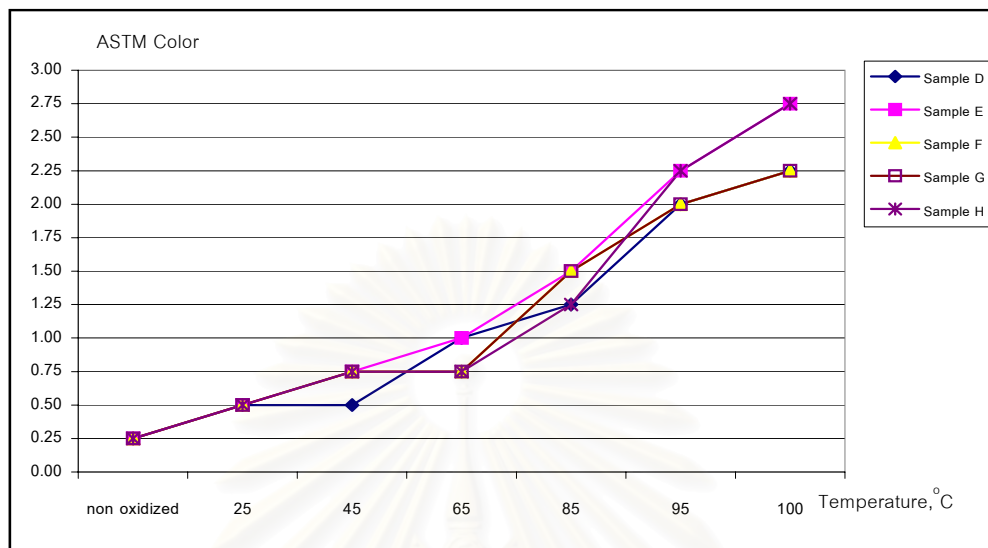


Figure 4-20 ASTM Color of diesel fuel after oxidation at various temperatures (varying in % component)

The results showed that since diesel fuels had different distribution of components, their response to oxidative stability would be diverse. It was clear that fuels having higher straight-run diesel fraction induced to longer induction period and to lower peroxide value. The opposite effects appeared in fuels having higher hydrocracked fraction sample induced to shorter induction period and to higher peroxide value. Figures 4 – 17 to 4-20, indicated that the component distribution was not direct effects on the stability of diesel fuel, but their stability depended on amount of natural inhibitor including sulfur and nitrogen heteroatom and upon aromatic or unsaturated compound. The effects concerned with total insoluble and color development would be explained as same as the sulfur, nitrogen and aromatic compound effects in 4.3.1, 4.3.2 and 4.3.3, respectively.

4.6. The impact of antioxidant additive on the stability of diesel fuel

(varying in various conditions)

4.6.1 Varying in the oxidation temperature

The impacts of various types of antioxidant additives on the stability of diesel fuel were investigated by at the same tested condition as previous section and compared with neat fuel. Sample D which having the ratio of heavy gas oil per light gas oil per hydrocracking gas oil of 65: 10: 25 was selected. Each 1 litre of sample D was added with 20 mg of additives A, B, C, D, E and F, respectively. Additives A and B are antioxidant, additive C is a metal deactivator additive and additive D is a lubricity and a dispersant additive. Additive E is a combined additive prepared from mixed additive A with additive B in the ratio 1:1, and additive F was prepared from additive A and D in same the ratio as additive E.

Each prepared sample was oxidized in the oxidation bomb which temperature was controlled at 25, 45, 65, 85, 95 and 100 ° C, respectively. The summary impacts of antioxidant additives on the stability of diesel fuel when the oxidation temperature was varied were shown in figures 4-21 to 4-24.

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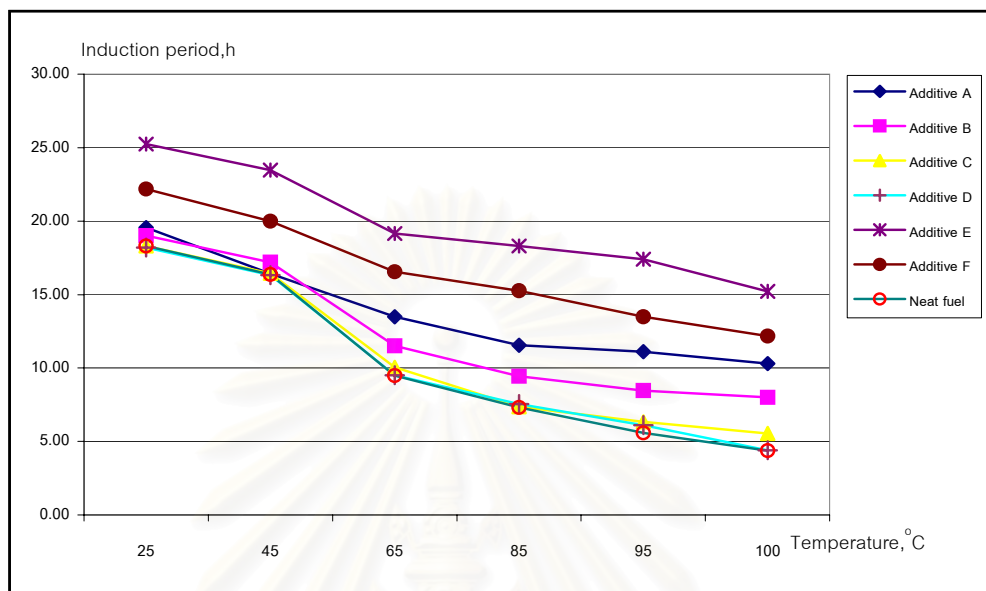


Figure 4-21 Induction period of diesel fuel blended with antioxidant additives after oxidation at various temperatures

Figure 4-21, indicated that the synthetic antioxidants were very effective in the increasing of induction period which was likely related to the time it induced a diesel fuel to build up radical concentrations to a steady state. They could slow and/or delay oxidation. These results also showed that the unadditized fuel (neat fuel) gave the most short induction period (4.17 hrs) after oxidation at 100 °C. While the sample D added with 20 mg/L of additive E which acted as an antioxidant gave the highest induction period (15.21 hrs). On the other hand, the sample added with additive D which a dispersant, showed the induction period for this run was slightly greater than the neat fuel.

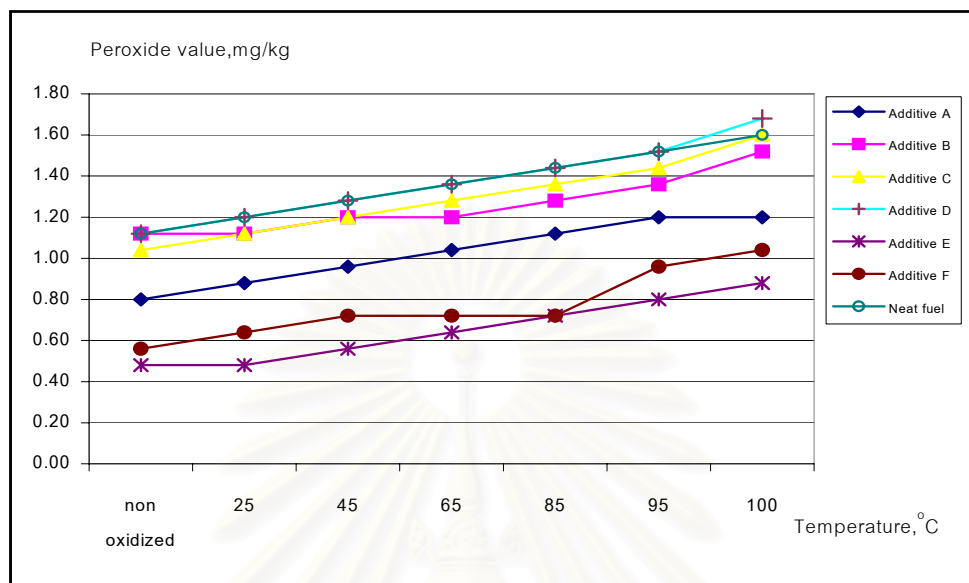


Figure 4-22 Peroxide value (PV) of diesel fuel blended with antioxidant additives after oxidation at various temperatures

Figure 4–22 showed the peroxide value measured by the modified ASTM D 3703 standard test method. The results indicated that all of antioxidant additives could decrease peroxides which was the primary oxidation products occurred via a series of free radical chain mechanism, concluded initiation propagation and termination step. The results suggested that the measured PV decrease under these conditions was reflection on the stability of the fuels. The low peroxide value related to low peroxides species occurring in fuels after oxidation. The fuels had low PV indicated that more stability. For example, the fuel added with additive E and F could decrease the peroxide value from 1.68 mg / kg to 0.88 and 1.04 mg/kg, respectively. The results explained that these additives could inhibit fuel oxidation. In the other hand, the sample added with additive D which acted as a

lubricity and a dispersant gave the peroxide value for this run was slightly less than the neat fuel. The sample added with additive C which acted as a metal deactivator (MDA) had little effect on reduction of peroxide value. A slight delay from the onset of oxidation was observed this sample. The MDA additive could prevent metal catalyzed reaction that produced free radicals. The results can be concluded that introducing of the synthetic antioxidant could delay in autoxidation during extended storage by increasing of the induction period and/or prevent peroxide formation. The effects of each additive on the stability of diesel fuel was conformed the order of additive $E > F > A > B > C > D$.

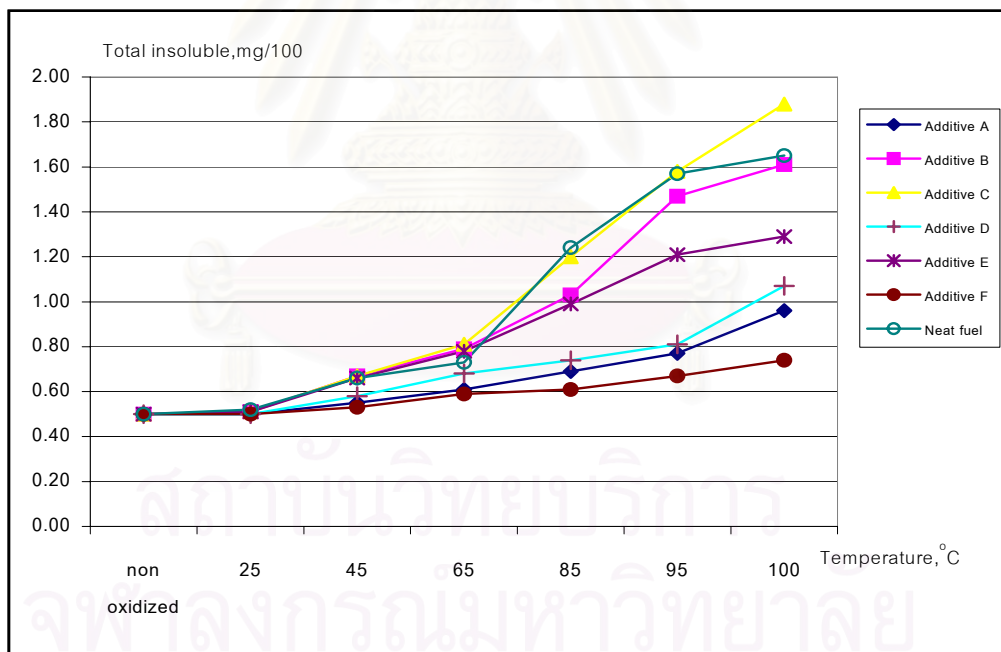


Figure 4-23 Total insoluble of diesel fuel blended with antioxidant additives after oxidation at the various temperatures

All of results explained that antioxidant additives have been postulated to play important roles in determining the oxidation behavior of blend fuel. Figure 4–23, showed that the introducing of the antioxidant additive could reduce the tendency for insoluble formation considerably in fuel samples. The antioxidant additives were very effective in elimination of the precursors that led to insoluble formation. Our studies showed that tendency of formation of total insoluble was a linear dependence with the temperature increased.

The results showed that the fuel blended with additive F was the most effective on decreasing of total insoluble formation. Metal deactivator additive (additive C) had little effect on decreasing of total insoluble produced after oxidation. The opposite effect appeared in fuel blended with additive D that resulted was efficiency on reducing total insoluble content predominantly. It could reduce from 1.65 to 1.07 mg/100 ml after oxidation at 100 ° C.

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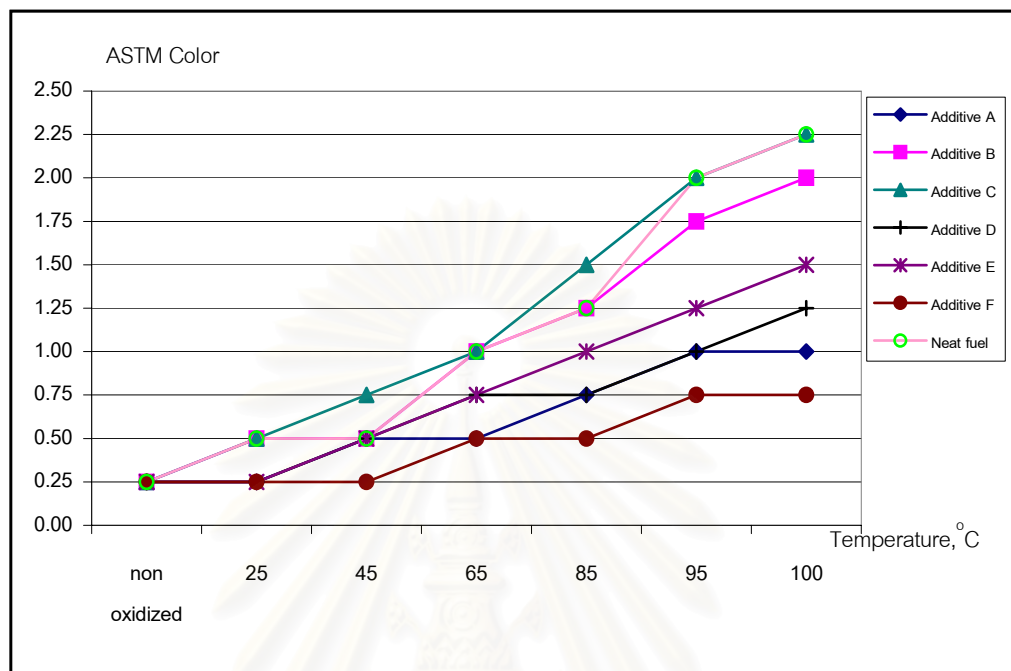
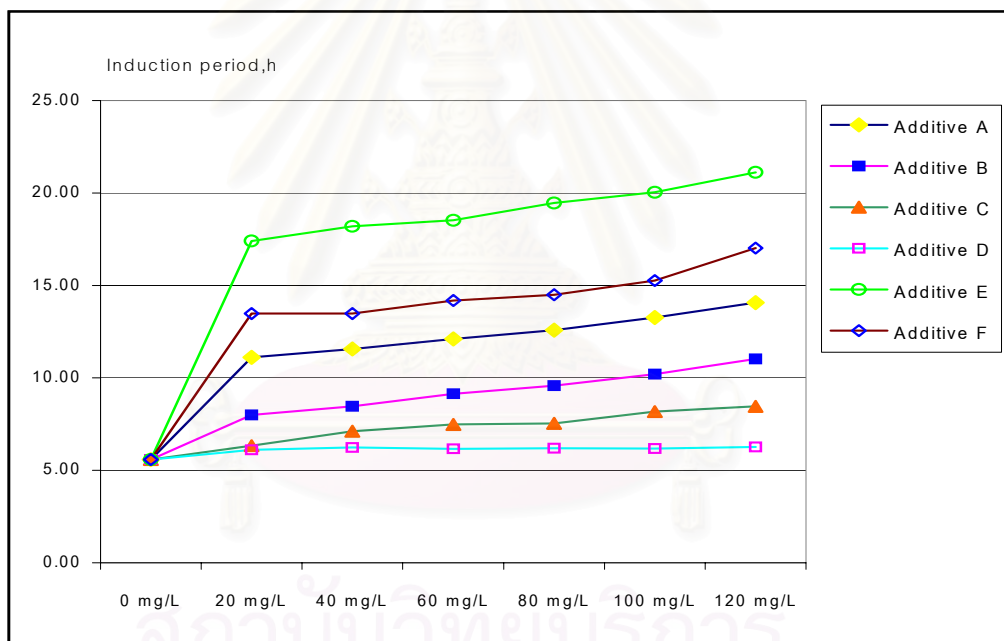


Figure 4-24 ASTM Color of diesel fuel blended with antioxidant additives after oxidation at various temperatures

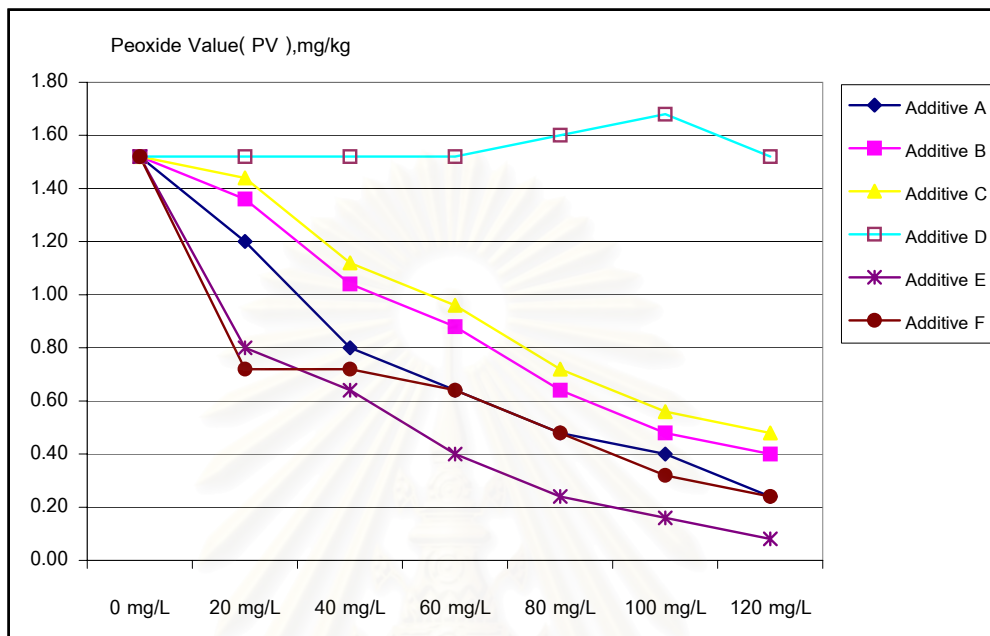
The results in figure 4–24 showed that additives A, D, E and F were significant influential on reducing color development of diesel fuels but additive B had little effect, and additive C had no effect on reducing color development. The ASTM color was reduced by antioxidant additive F from 2.25 to 0.75 after oxidation at 100 °C. A significant improvement in color was observed for the other additives also.

4.6.2 Varying in the concentration of antioxidant additives

The dependence of diesel fuel stability on antioxidant concentration was studied extensively in oxidation bomb at room temperature up to 100 ° C. The extended effects of antioxidant concentration in autoxidation was reported base on plot of [antioxidant] versus induction period, peroxide value, total insoluble and ASTM Color, respectively. The results of the concentration effects on the stability of diesel fuel are shown in figures below.



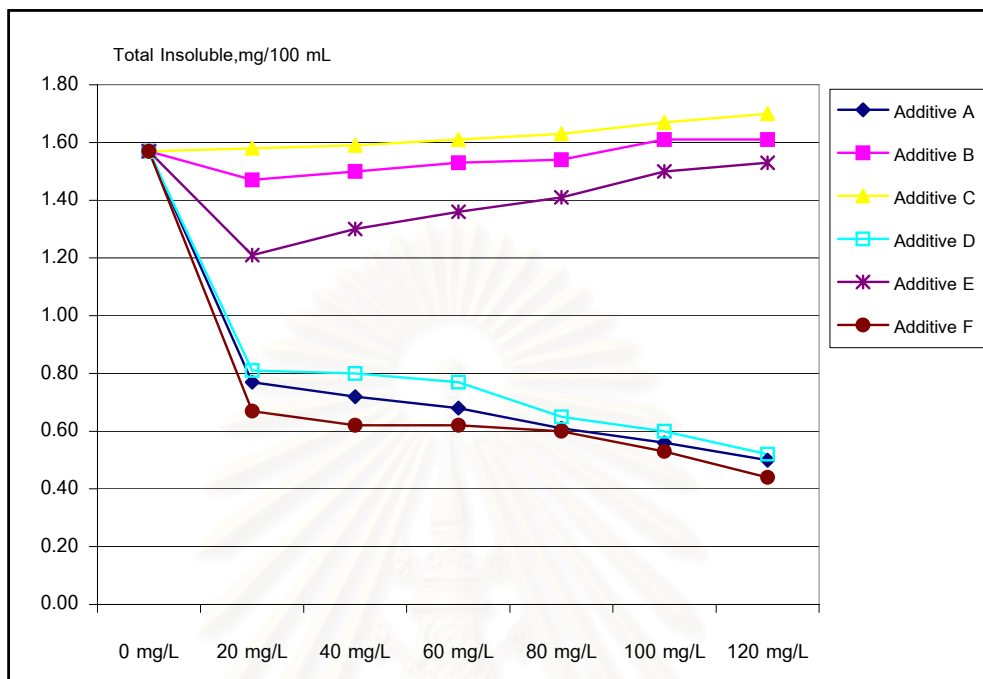
**Figure 4-25 Induction period of diesel fuel after oxidation at 95 °C
(varying in the concentration of antioxidant additives)**



**Figure 4-26 Peroxide value (PV) of diesel fuel after oxidation at 95 ° C
(varying in concentration of antioxidant additives)**

From the results in the figures 4-25 to 4-26, it was clear that these primary antioxidants retarded the oxidation reaction either with very different efficiencies or by different mechanism. Fuel sample blended with additives A, B, E and F displayed progressively longer induction period in oxidation when antioxidant concentration was increased. In figure 4-25, the results showed that additives C and D were not same effective in delaying oxidation as additives A, B, E and F at a given concentration. They had little effects on increasing of the induction period of diesel fuel. For example 100 mg /l of additive E offered a 20.04 hrs delay while the same concentration of additives C and D gave a 8.18 and 6.18 hrs delay,

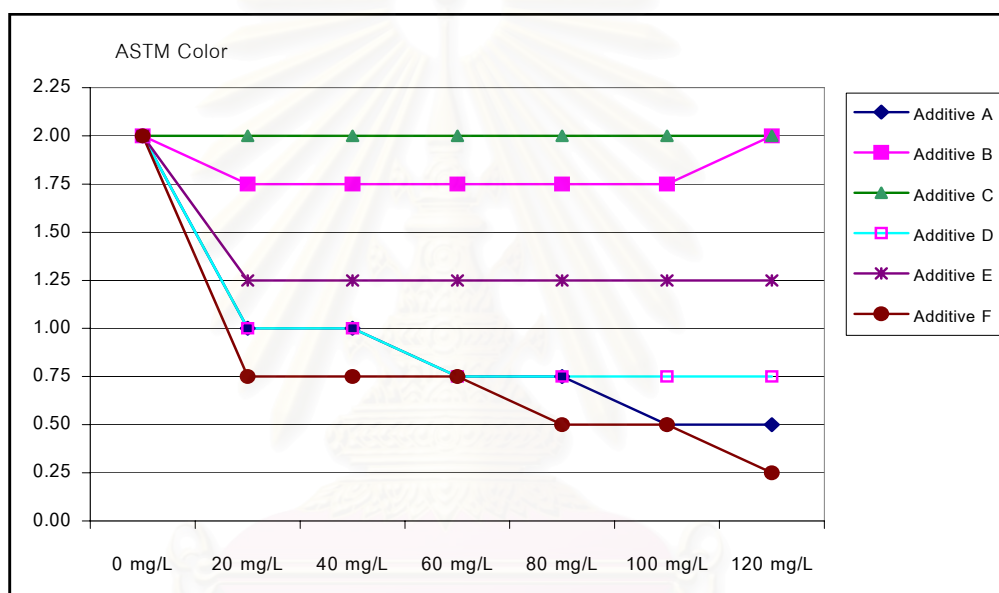
respectively. The concentration of antioxidant was associated with induction period, observed induction period increased approximately linearly with additive concentration. The result in figure 4 –25 was associated with the results in figure 4 –26 concerned with the effects of antioxidant concentration on peroxide value decreased. The results indicated that five antioxidant additives displayed the observed peroxide value of sample after oxidation at 95 °C decreased approximately linearly with additive concentration. Exception of additive D, showed that it had no effect on decreasing of peroxide formation. At the same concentration, amine type antioxidant (additive A) had more efficiency on increasing of the induction period and on reducing of PV than phenol type antioxidant (additive B). Additive B had no net or slightly decreasing in peroxide species occurred during oxidation. The results also demonstrated that the efficiency of antioxidant and metal deactivator additive increased when concentration increased, but dispersant additive had no benefit when concentration was increased.



**Figure 4-27 Total insoluble of diesel fuel after oxidation at 95 °C
(varying in concentration of antioxidant additives)**

Figure 4–27, showed that the effects of antioxidant concentration on decreasing of total insoluble formation, the results found that three additives displayed progressively lower deposit formation in oxidation when antioxidant concentration increased. For additive A, D and F, the reduction of total insoluble content were achieved with antioxidant concentration to 20 mg/ l. The observed total insoluble was reduced from 1.57 mg/100 ml to 0.77, 1.47, 1.58, 0.81,1.21 and 0.67 mg/100 ml when added with 20 mg/l of additive A, B, D, E and F, respectively. At high concentration of additives, the results also indicated that additive B, C and E had no efficiency to minimized total insoluble, but they gave

opposite results. These data could support the mechanism of autoxidation in 4.7 that the major termination reaction was the major production pathway for total insoluble. The total insoluble formation was increased approximately linearly with additive concentration. So, can be proposed that additive B, C and E had no effect on reducing of the total insoluble that occurred during oxidation.



**Figure 4-28 ASTM Color of diesel fuel after oxidation at 95 °C
(varying in concentration of antioxidant additives)**

The effects of additive concentration on the color development of diesel fuel was shown in figure 4–28, the results showed that the tendency of ASTM color reduce related to total insoluble decreased. Additive A, D and F could reduce ASTM color from 2.0 to less than 1.25, 1.0 and 0.75, respectively. They also gave more efficiency to reduce ASTM color when concentration was

increased. Additive C displayed no effect on the color development while additive B displayed was slightly color developed less than the neat fuel. All of results, concluded that different type of antioxidant could retard the oxidation by different efficiency and/or by different mechanism.

4.6.3 Varying in the concentration of N, S –heteroatom containing

In this case, three diesel fuel samples which had different N, S-heteroatom content (see table 3-1) were selected to evaluate the effects of antioxidant additive on diesel fuel stability. The results of the impact of the antioxidant additive to improve diesel fuel stability when varied in N,S heteroatom containing were shown in the figures 4-29 to 4-32 below.

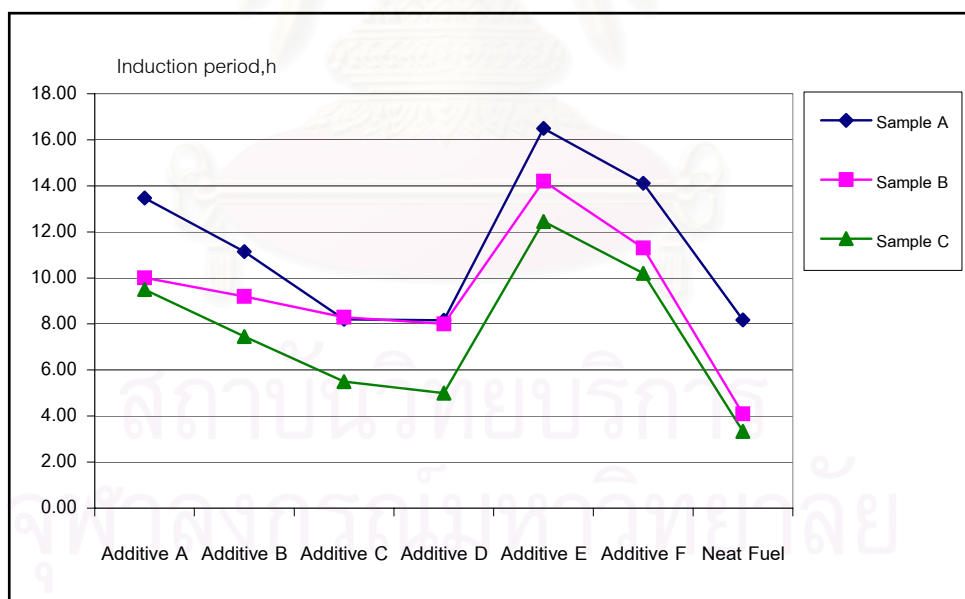


Figure 4-29 Induction period of tested samples added with 20 mg/l of various antioxidant additive types after oxidation at 95 ° C

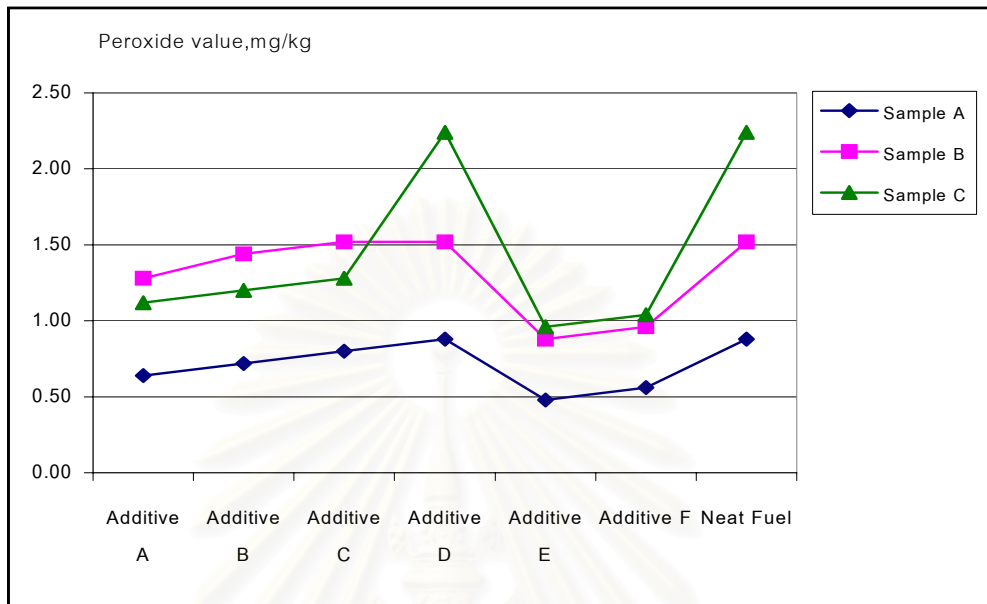


Figure 4-30 Peroxide value (PV) of tested samples added with 20 mg/l of various additive types after oxidation at 95 ° C

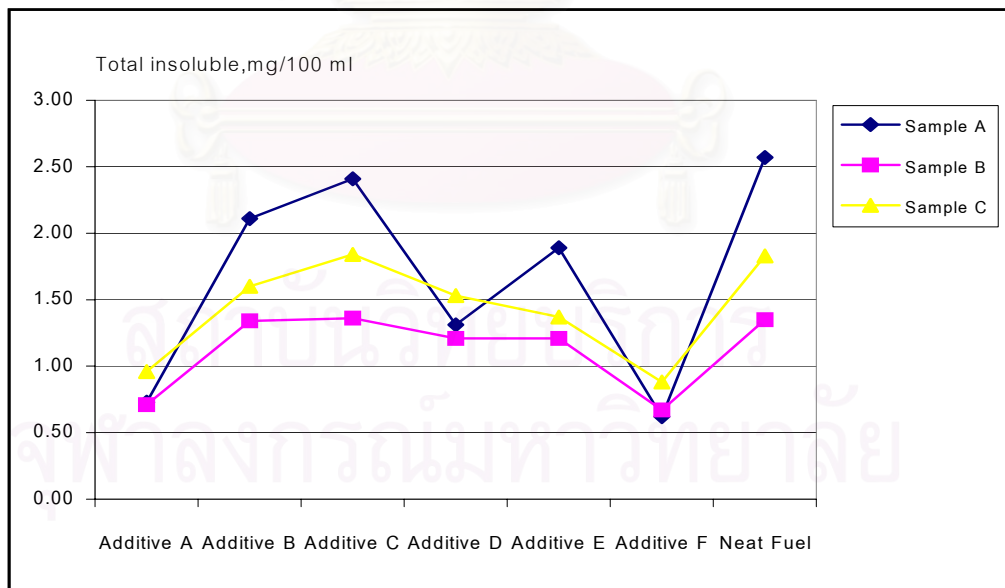


Figure 4-31 Total insoluble of tested samples added with 20 mg/l of various additive types after oxidation at 95 ° C

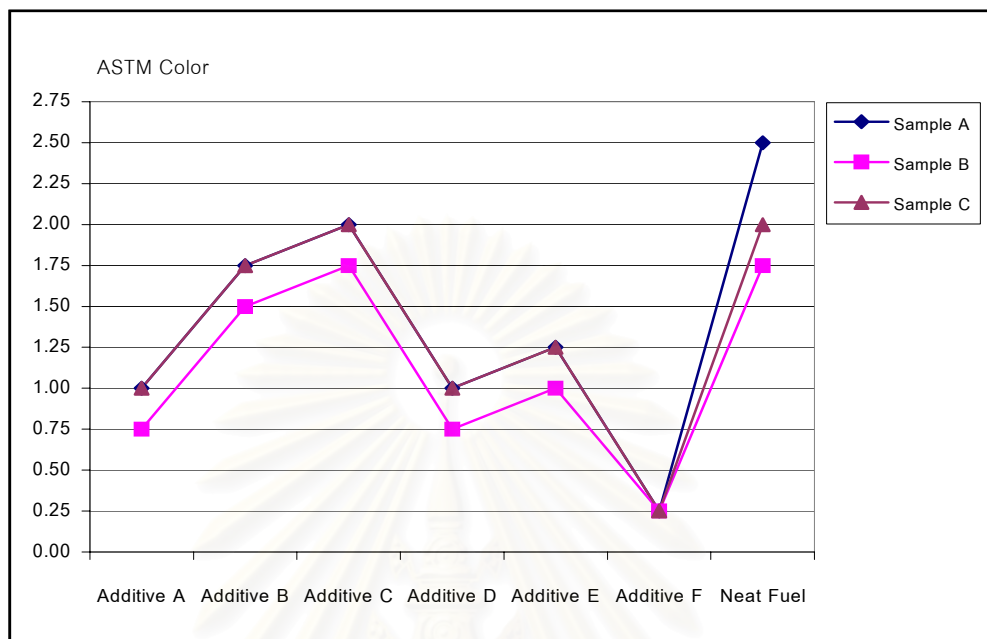


Figure 4-32 ASTM Color of tested samples added with 20 mg/l of various additives types after oxidation at 95 ° C

The results showed that all of additives had more effective to improve stability in the fuel samples which having low concentration of N, S-heteroatom than fuel samples having high concentration of N, S-heteroatom. For sample A, an antioxidant was generally ineffective to increase induction period and to reduce peroxide value. The fuel already contained many natural antioxidant, (N, S-heteroatom) that contributed to its inherently slow oxidation rate. An antioxidant can be used to hold insoluble deposition products in solution by preventing agglomeration and to control color development to be no darker than specification. On the other hand, sample C which was a hydrotreated diesel fuel consumed oxygen rapidly but produced little total insoluble under oxidation at

this condition. Sample C contained very few naturally occurring antioxidant, and concentration of sulfur was low. An antioxidant would generally be beneficial for this type of fuel. It would be effective in delaying oxidation thereby delaying any insoluble formation that occurred and also controlled color development must to be no darker than specification.

4.6.4 Varying in the component distribution and density

Each 1 l of diesel samples with different in component content and density were added with 20 mg of each antioxidant additive. Then, the samples were oxidized at 95 °C until breakpoint was reached. The induction period, total insoluble, peroxide value (PV) and ASTM color were investigated. These properties can be identification of the impacts of antioxidants on the stability of diesel fuel when component distribution and density were varied. The results of these effects were shown in the figures 4-33 to 4-36 below.

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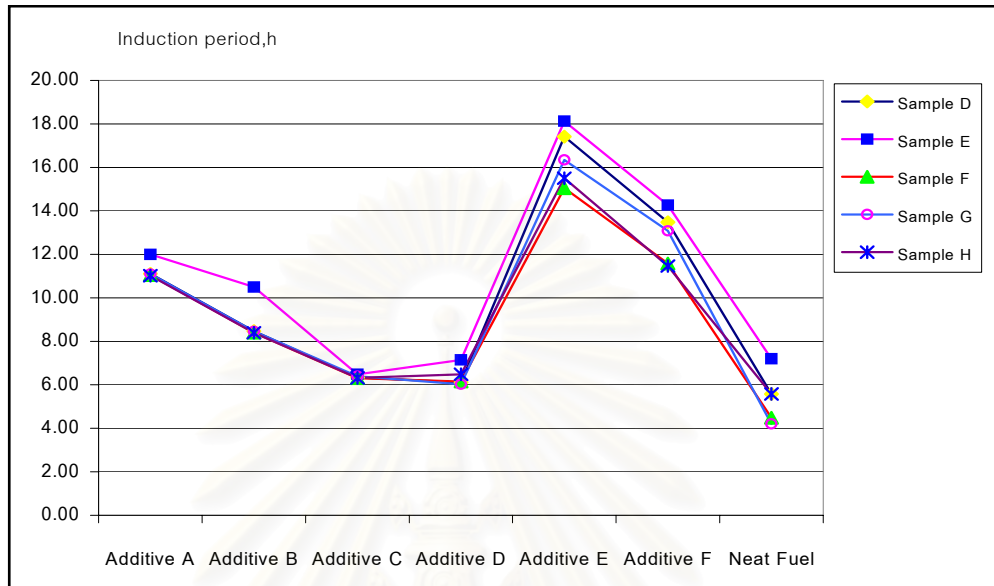


Figure 4-33 Induction period of diesel fuel blended with antioxidant additives after oxidation at 95 °C(varying in % component and density)

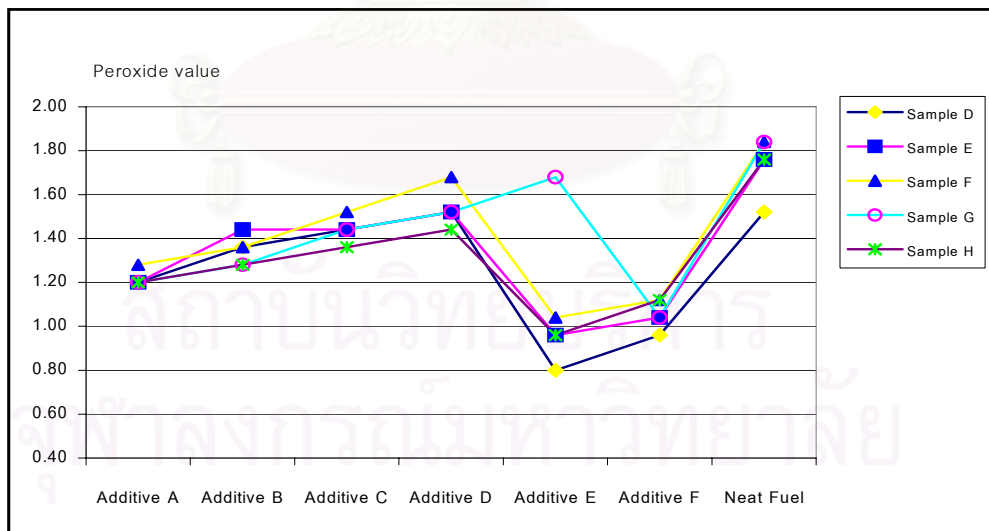


Figure 4-34 Peroxide value(PV)of diesel fuel blended with antioxidant additives after oxidation at 95 °C(varying in % component and density)

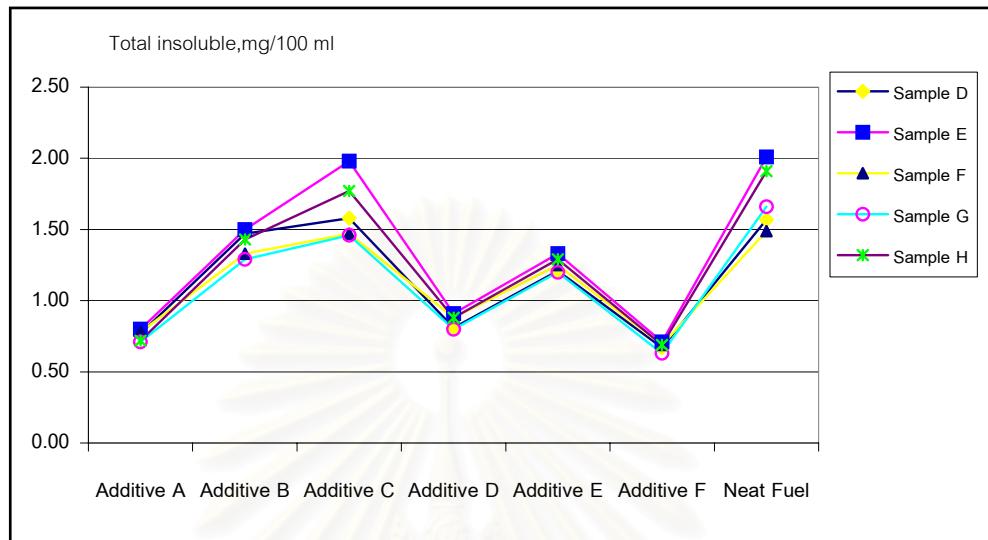


Figure 4-35 The Total insoluble of diesel Fuel blended with antioxidant additives after oxidation at 95 °C(varying in % component and density)

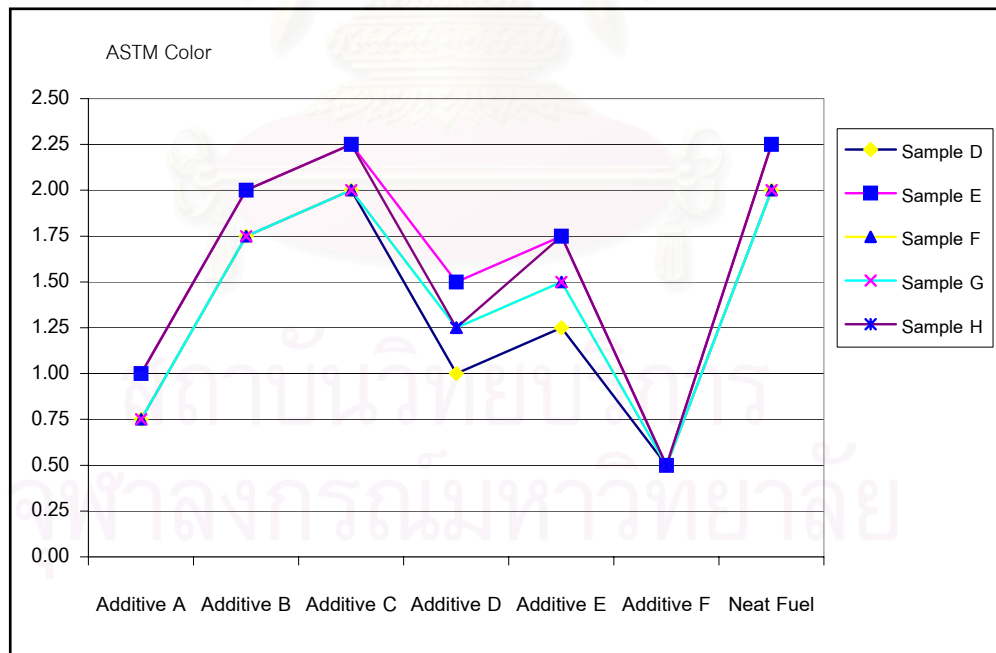
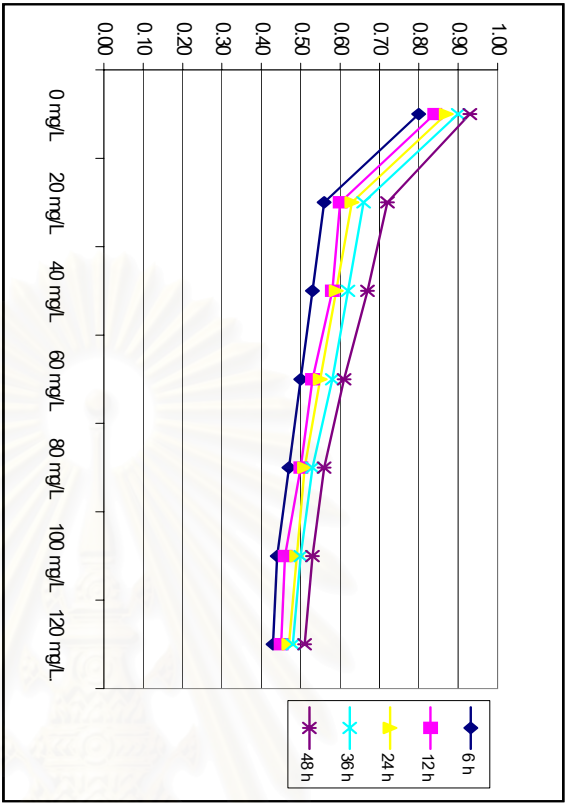


Figure 4-36 ASTM Color of diesel fuel blended with antioxidant additives after oxidation at 95 °C(varying in % component and density)

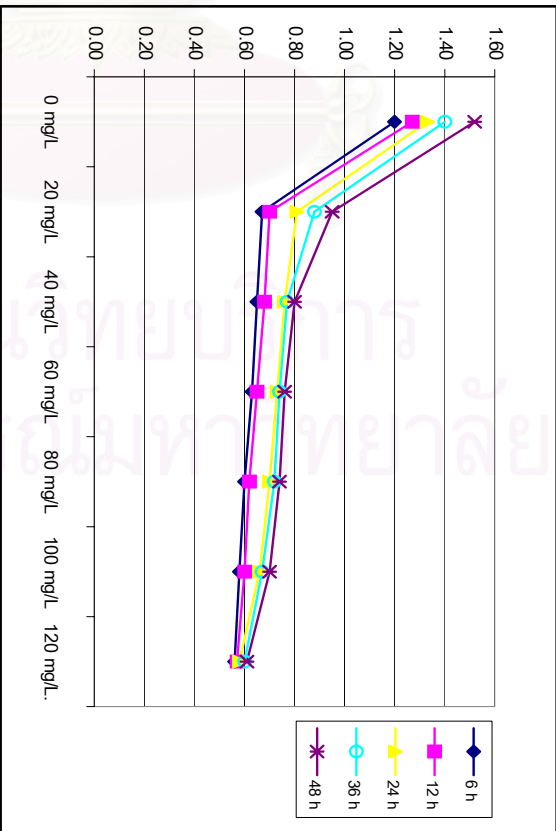
The results in figures 4-33 to 4-36 indicated that component distribution and density of fuel sample were indirectly influence on the effective of antioxidant additives. The samples F and H which had high levels of hydrocracked gas oil fraction gave more effect than other fuel which had low levels of hydrocracking gas oil fraction. These data indicated that the chemical precursors responsible for instability of diesel fuels were predominantly in hydrocracked gas oil. Hydrocracked gas oil had high levels of aromatic compound and the concentration of the natural antioxidant (N, S- heteroatom) was reduced by hydrotreatment, led to enhancement of all primary antioxidant efficiency. Antioxidant additives had effectively eliminated precursors, which induced to the formation of insoluble, could delay oxidation and controlled color development in diesel fuel to be no darker than specification. Therefore diesel fuels with high levels of hydrocracking fraction required synthetic antioxidant to limit autoxidation during extended storage.

4.6.5 Varying in the reaction time

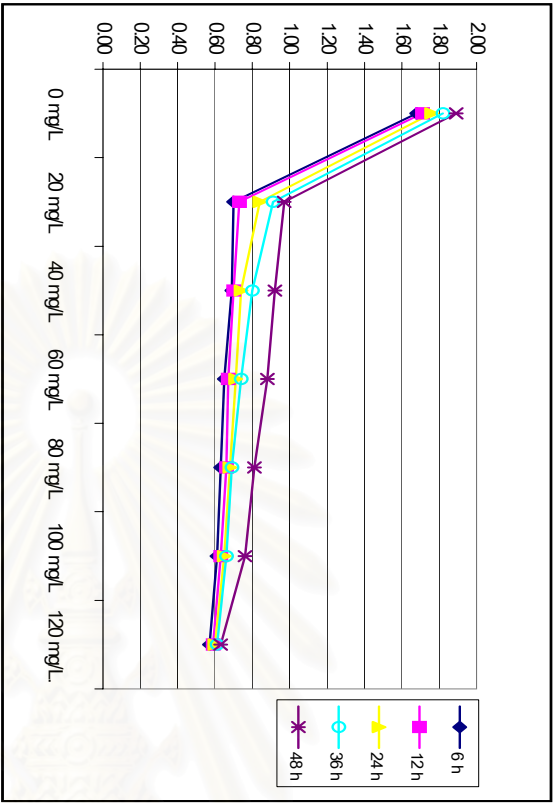
The sample D which was a representative of diesel fuel for sale was selected to investigate the total insoluble formation when the reaction time for oxidation was varied. The total insoluble was one of characteristic properties as indication of the ability of the antioxidant additive to improve diesel stability after oxidation at the test conditions followed in table 3 – 5. The amount of total insoluble was determined after cooling for about 2 h. The impact of each antioxidant additives in tested samples were shown in the figures below.



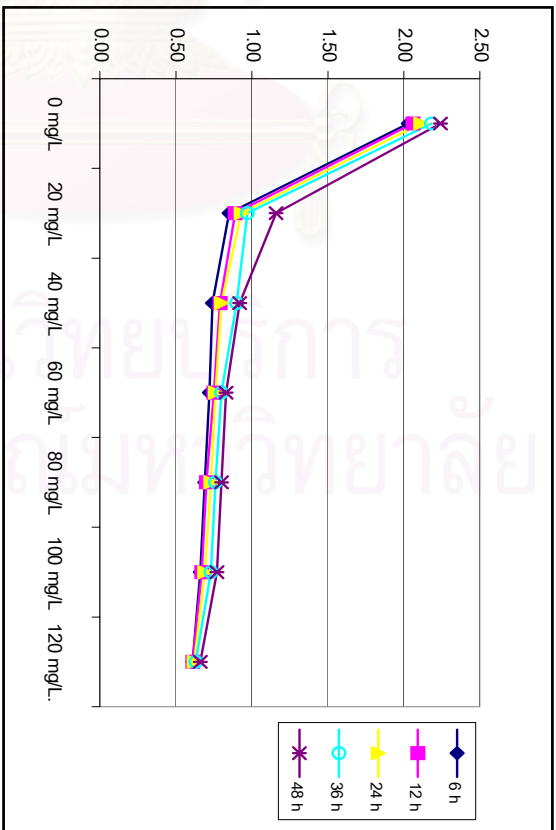
4-37c Total insoluble of diesel fuel added with additive A after oxidation at 65 °C



4-37d Total insoluble of diesel fuel added with additive A after oxidation at 85 °C

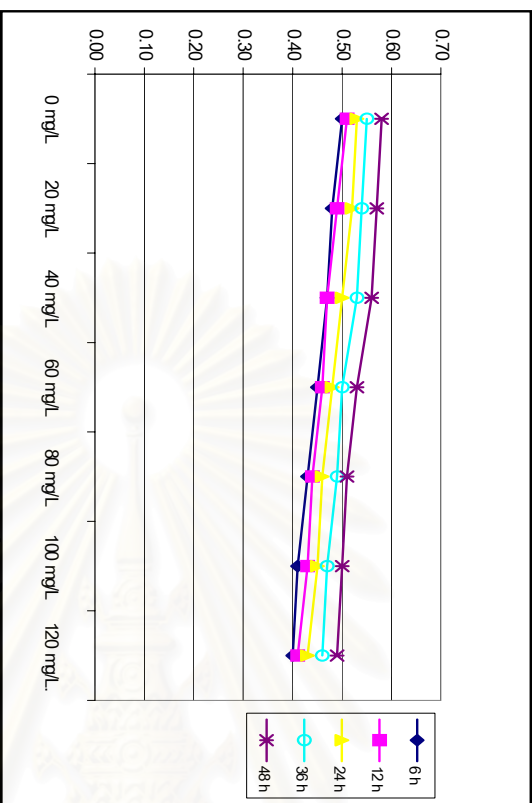


4-37 e Total insoluble of diesel fuel added with additive A after oxidation at 95 ° C

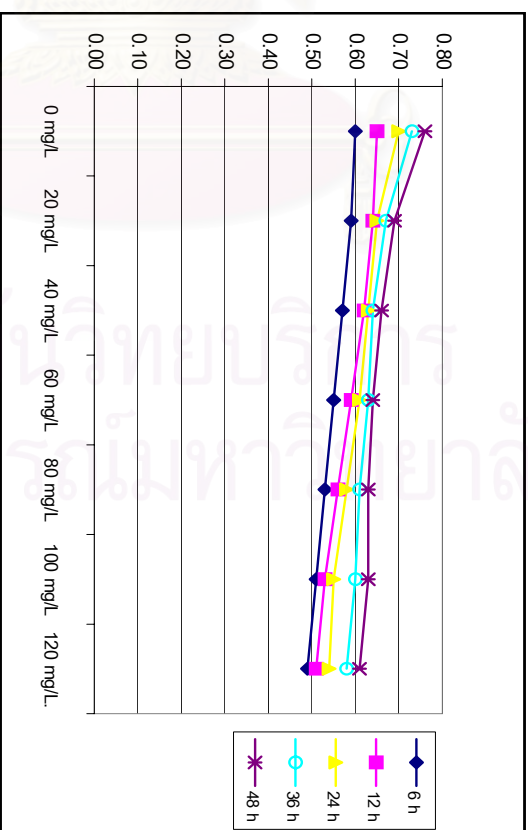


4-37 f Total insoluble of diesel fuel added with additive A after oxidation at 100 ° C

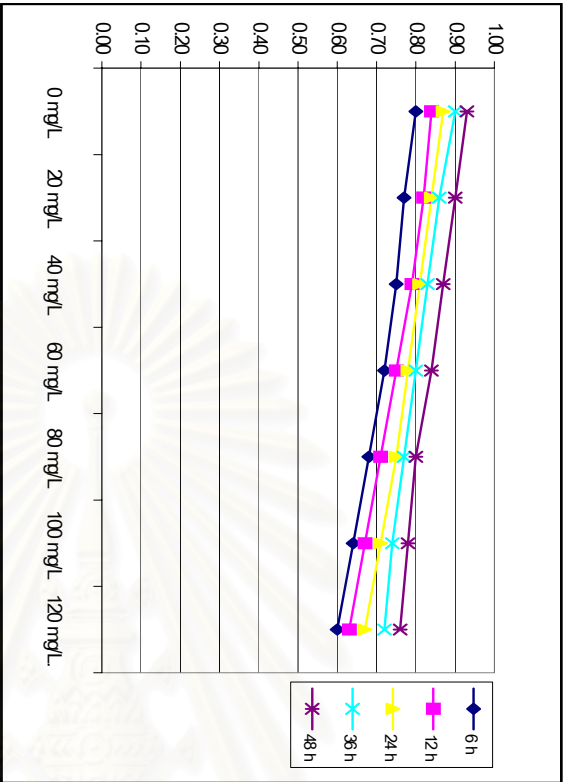
Figure 4-37 Total insoluble of diesel fuel added with the additive A after oxidation at various reaction times



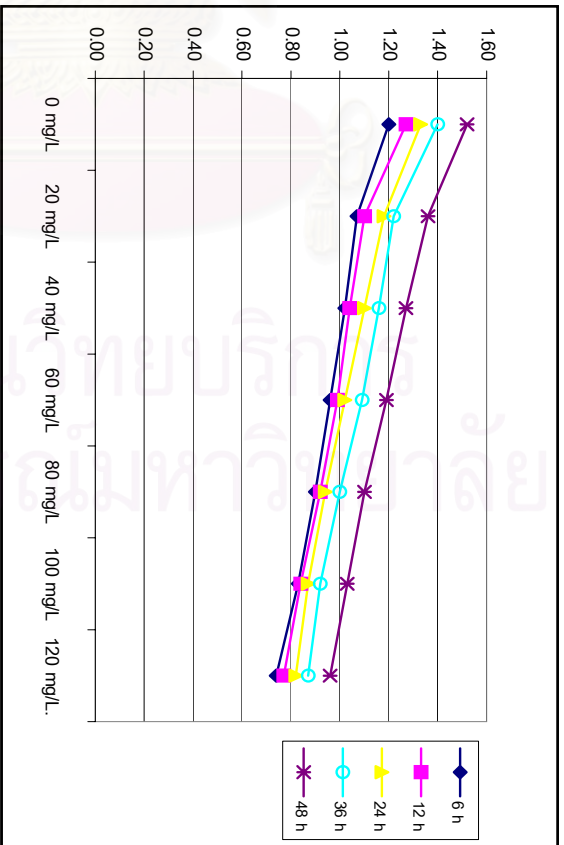
4-38 a Total insoluble of diesel fuel added with additive B after oxidation at 25 ° C



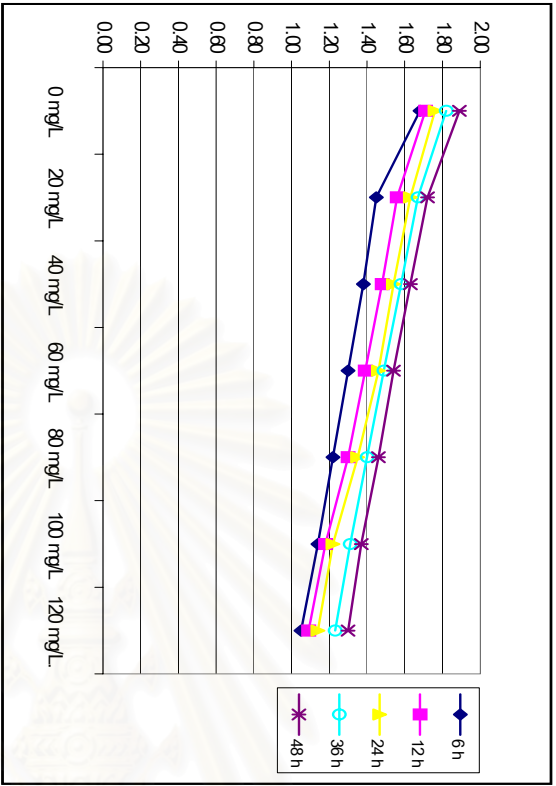
4-38b Total insoluble of diesel fuel added with additive B after oxidation at 45 ° C



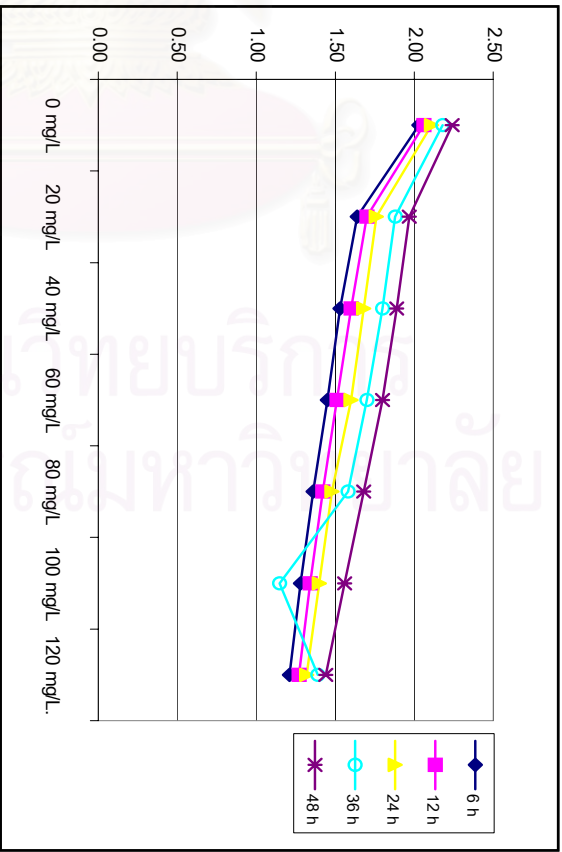
4-38c Total insoluble of diesel fuel added with additive B after oxidation at 65 ° C



4-38 d Total insoluble of diesel fuel added with additive B after oxidation at 85 ° C

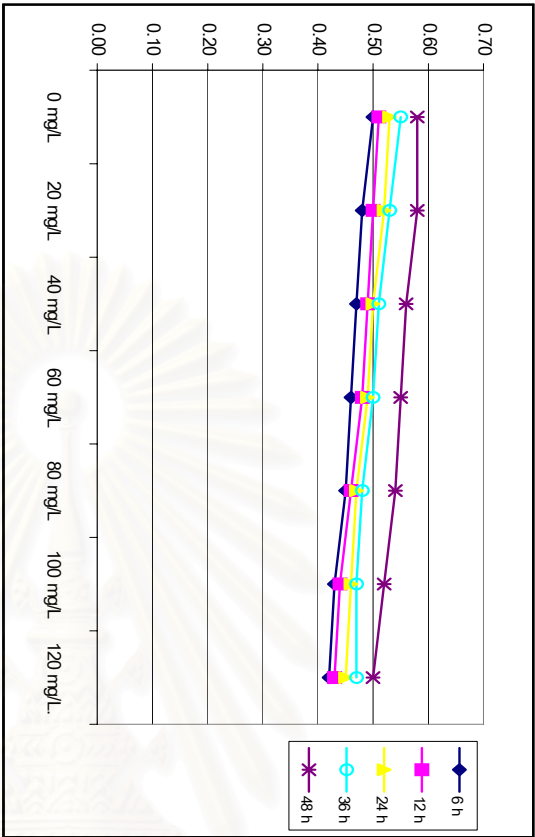


4-38 e Total insoluble of diesel fuel added with additive B after oxidation at 95 ° C

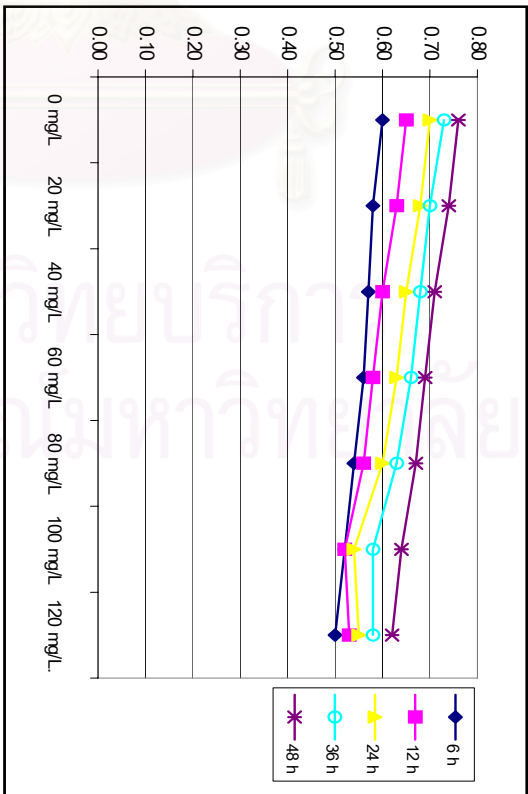


4-38f Total insoluble of diesel fuel added with additive B after oxidation at 100 ° C

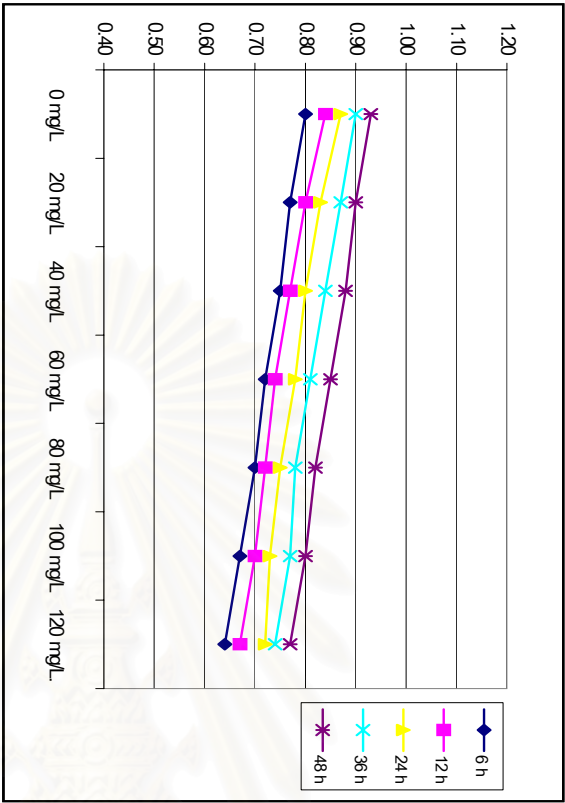
Figure 4-38 Total insoluble of diesel fuel added with the additive B after oxidation at various reaction times



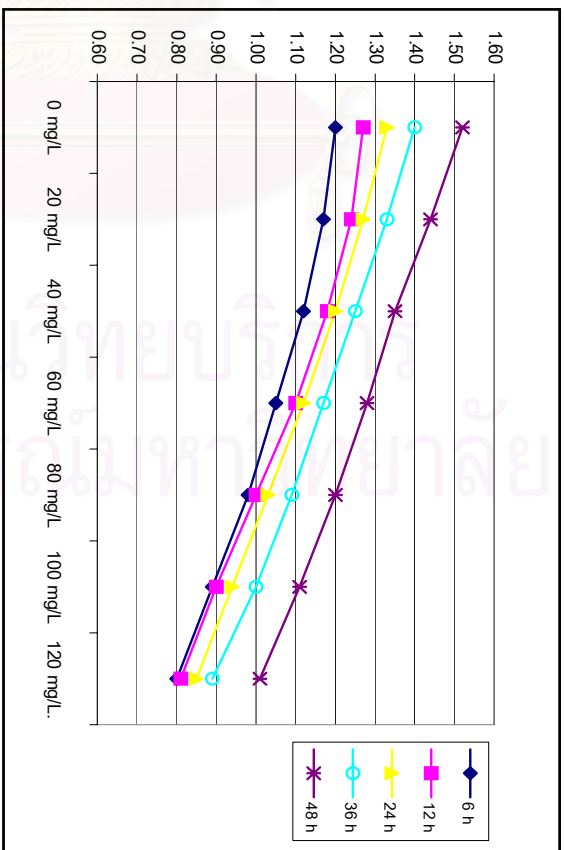
4-39 a Total insoluble of diesel fuel added with additive C after oxidation at 25° C



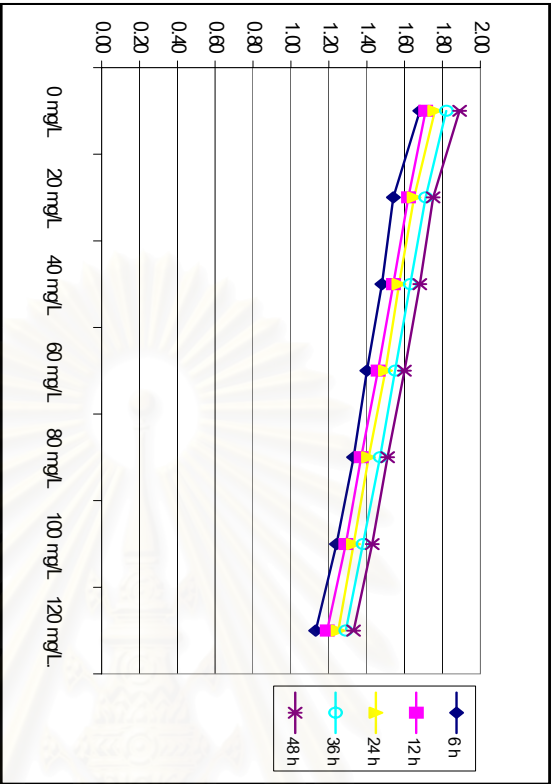
4-39 b Total insoluble of diesel fuel added with additive C after oxidation at 45° C



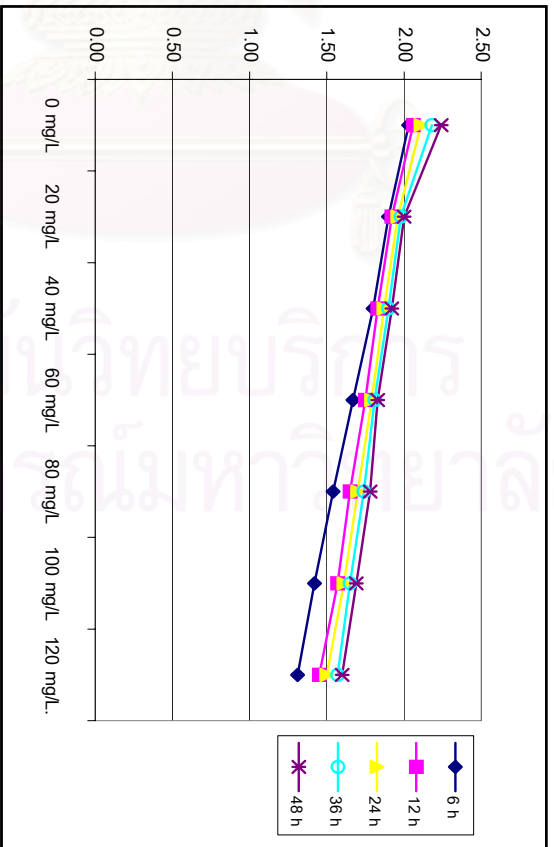
4-39 c Total insoluble of diesel fuel added with additive C after oxidation at 65 ° C



4-39d Total insoluble of diesel fuel added with additive C after oxidation at 85 ° C

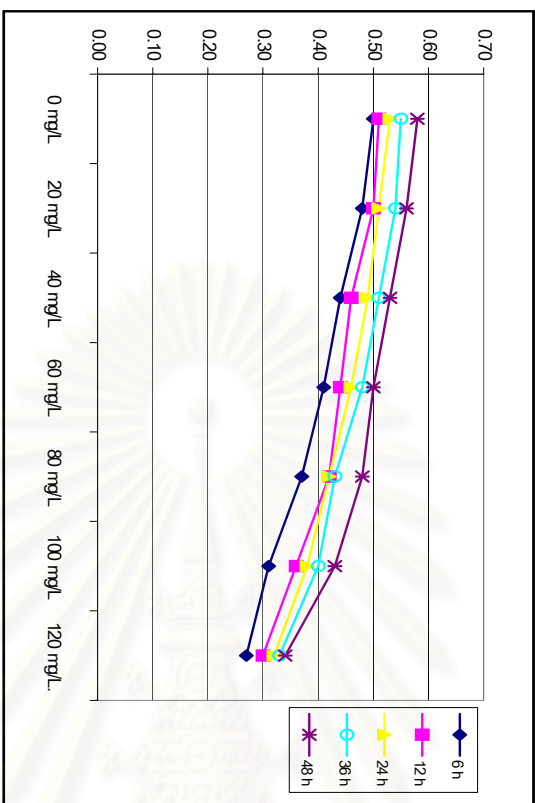


4-39 e Total insoluble of diesel fuel added with additive C after oxidation at 95 ° C

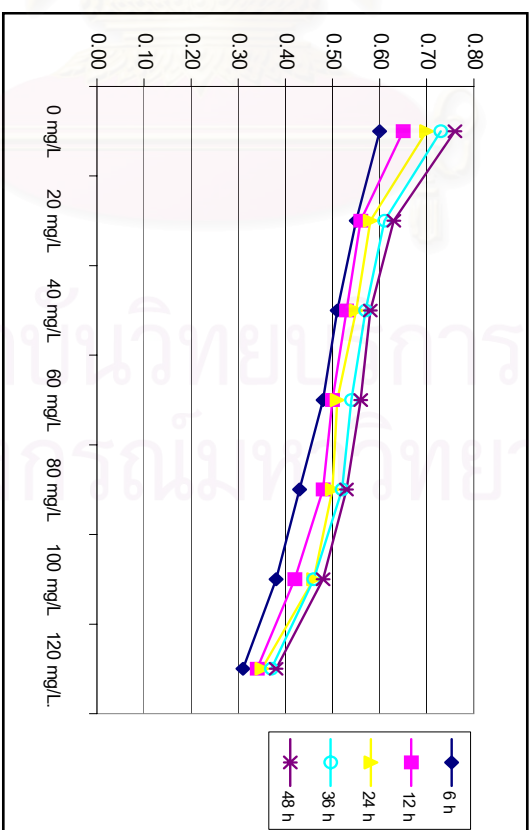


4-39 f Total insoluble of diesel fuel added with additive C after oxidation at 100 ° C

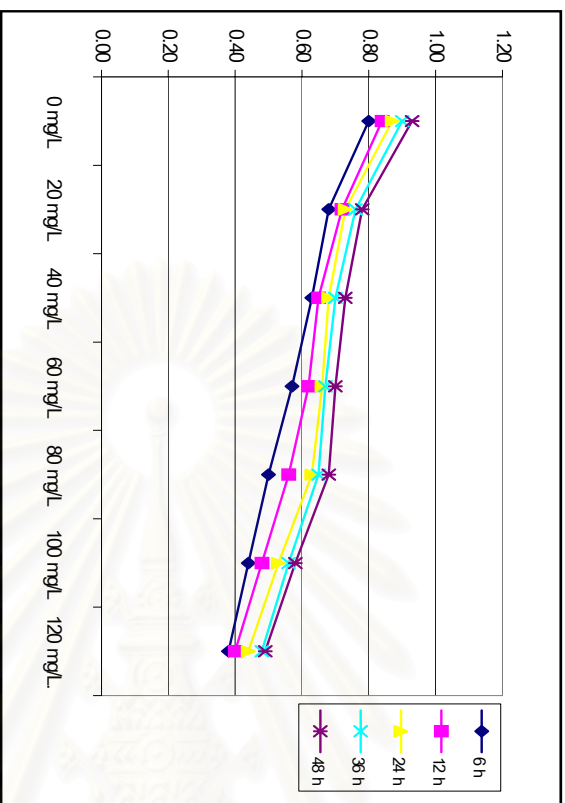
Figure 4-39 Total insoluble of diesel fuel added with the additive C after oxidized at various reaction times



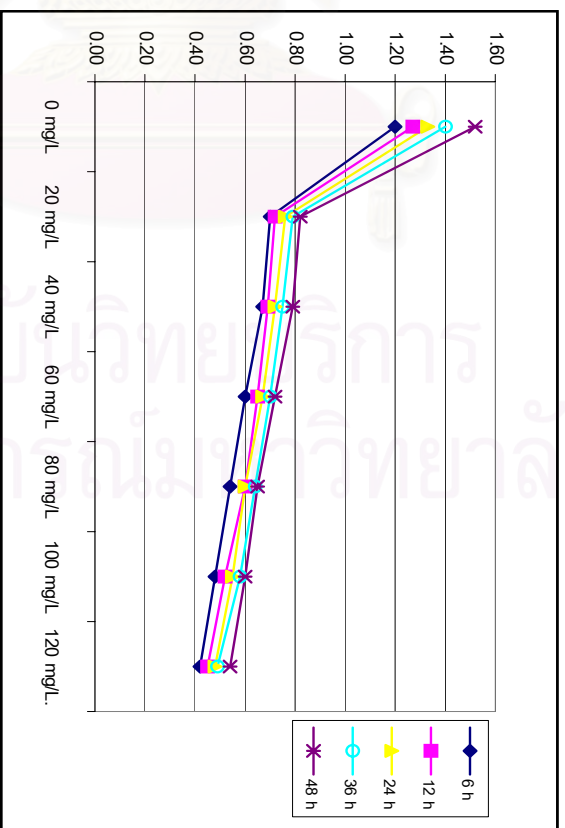
4-40 a Total insoluble of diesel fuel added with additive D after oxidation at 25 ° C



4-40 b Total insoluble of diesel fuel added with additive D after oxidation at 45 ° C



4-40 c Total insoluble of diesel fuel added with additive D after oxidation at 65 ° C



4-40 d Total insoluble of diesel fuel added with additive D after oxidation at 85 ° C

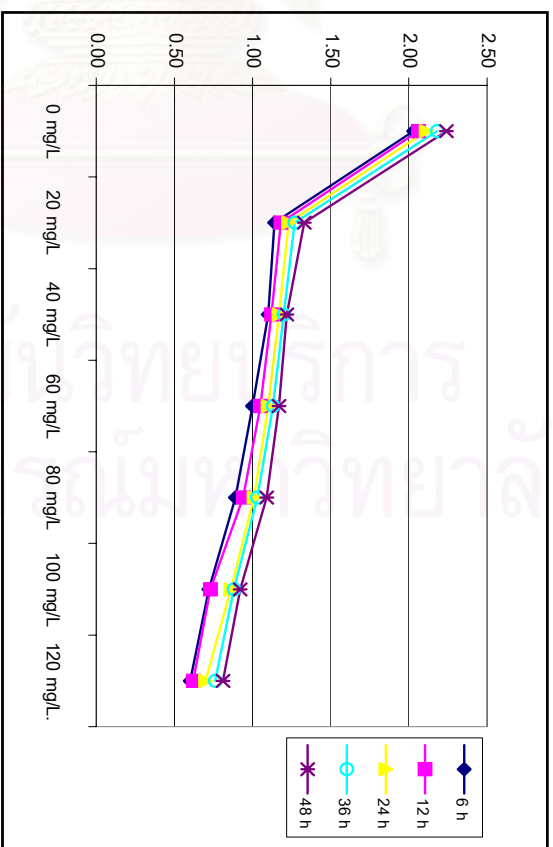
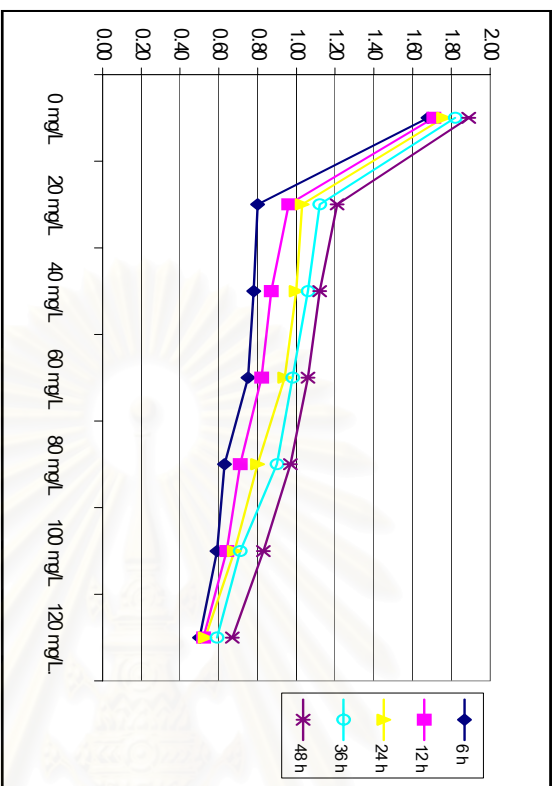
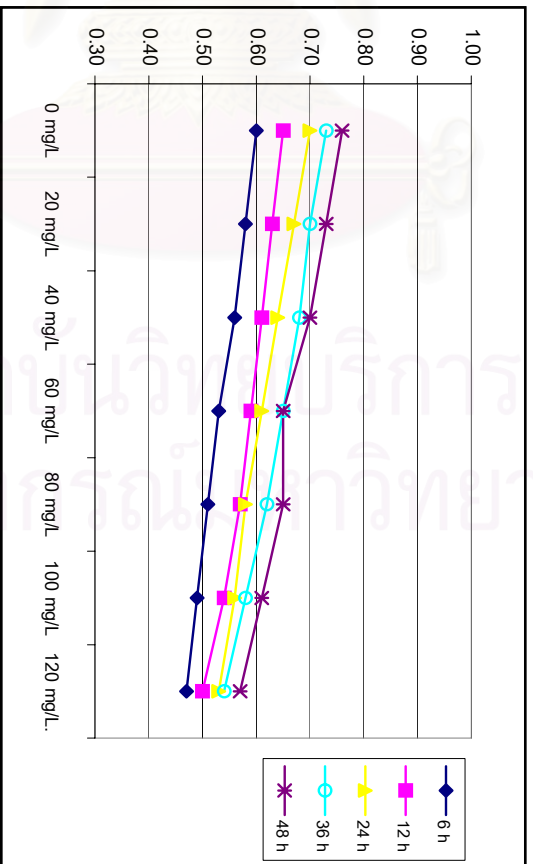
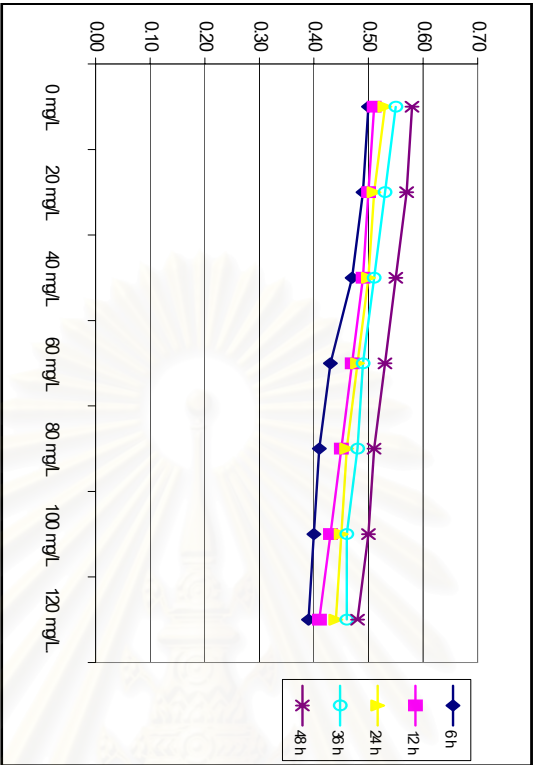
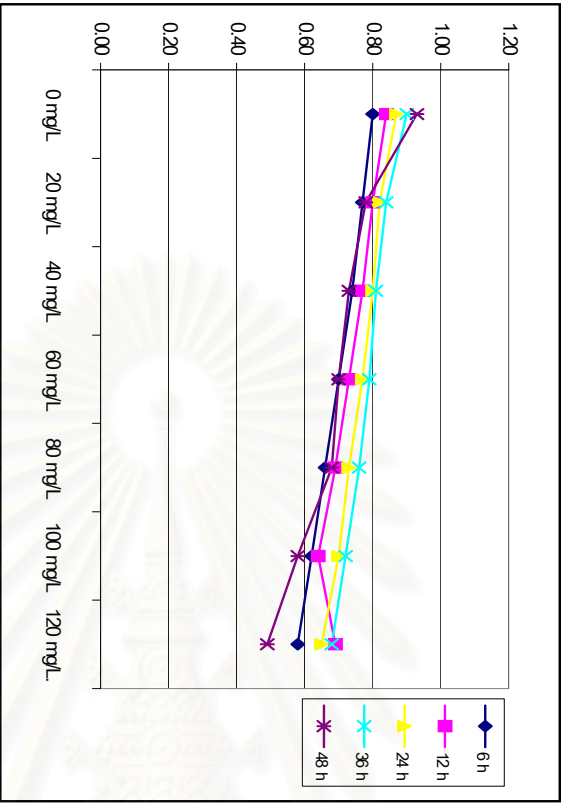
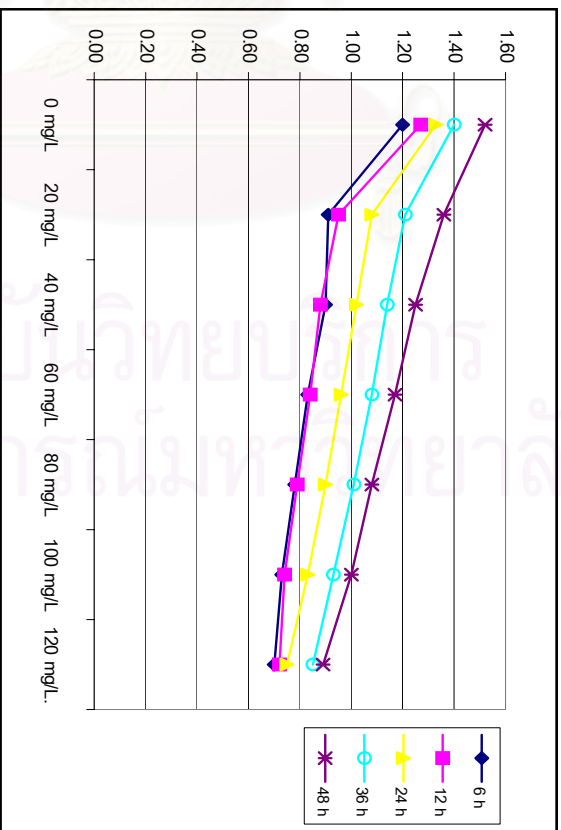


Figure 4-40 Total insoluble of diesel fuel added with the additive D after oxidation at various reaction times





4-41c Total insoluble of diesel fuel added with additive E after oxidation at 65 ° C



4-41 d Total insoluble of diesel fuel added with additive E after oxidation at 85 ° C

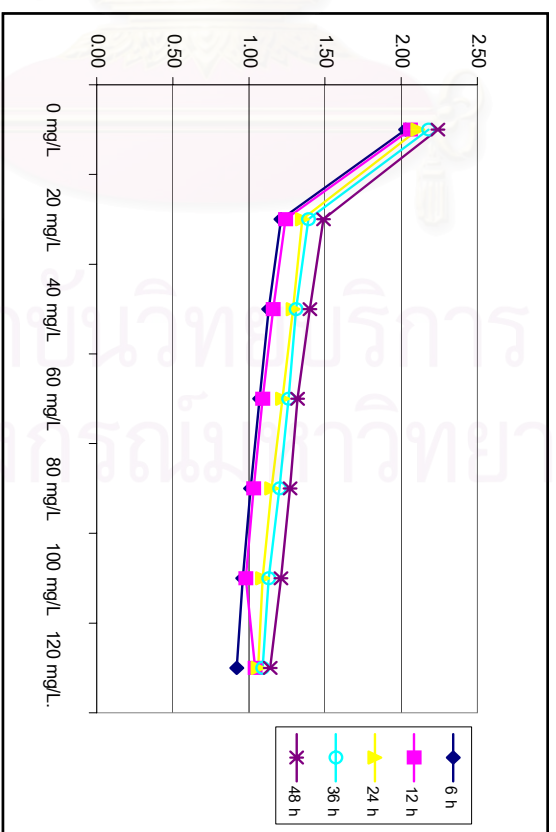
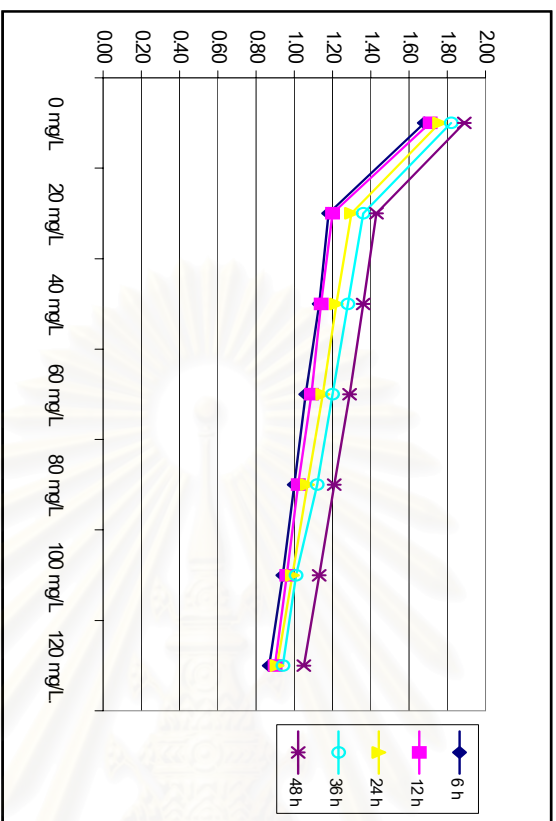
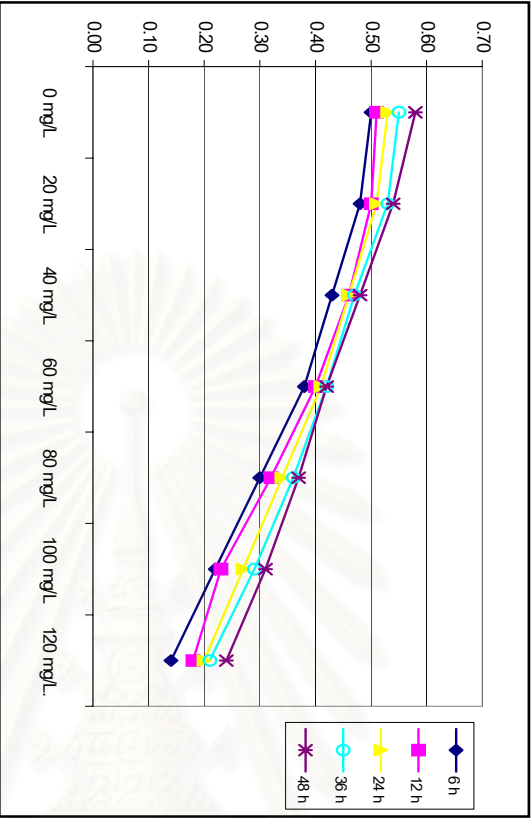
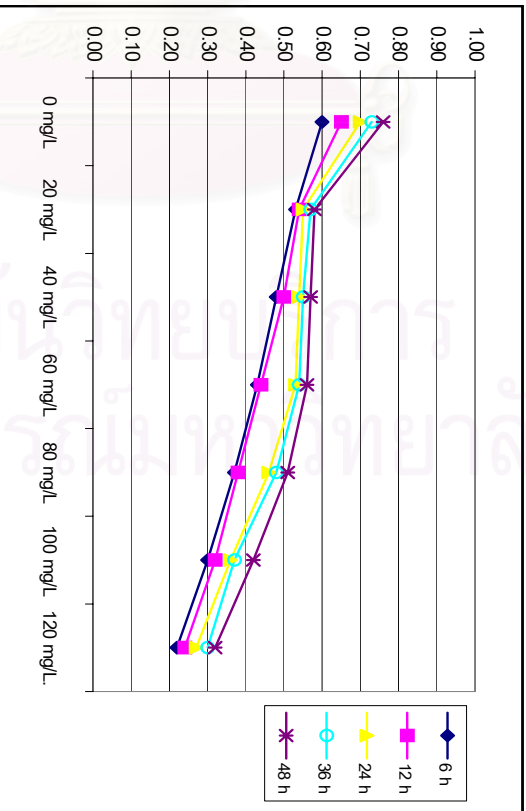


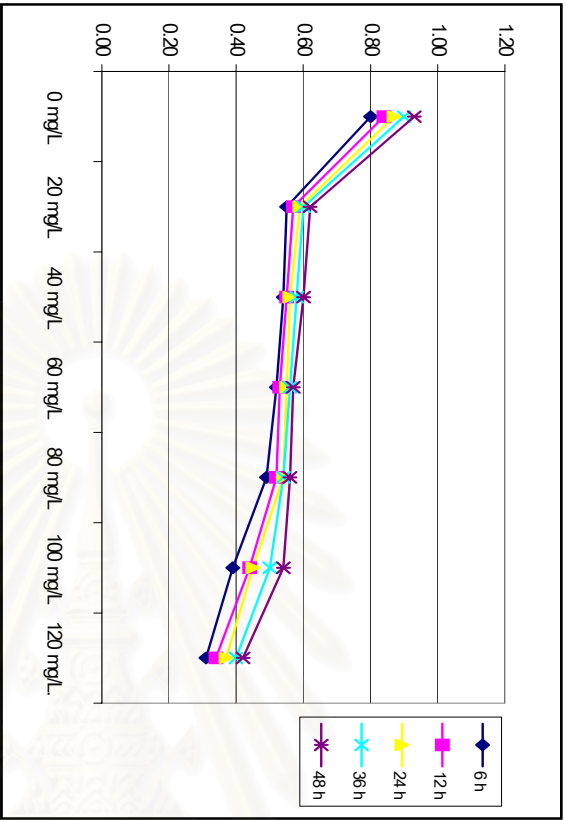
Figure 4-41 Total insoluble of diesel fuel added with the additive E after oxidation at various reaction times



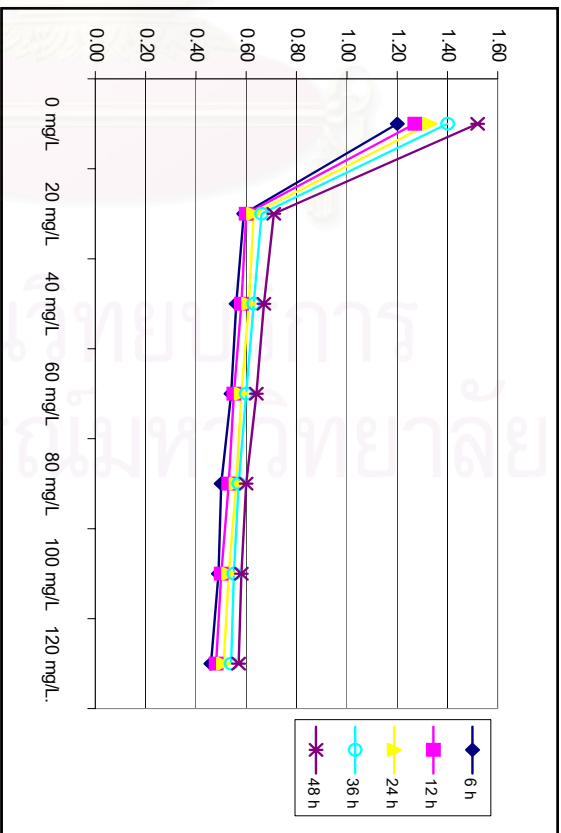
4-42 a Total insoluble of diesel fuel added with additive F after oxidation at 25 ° C



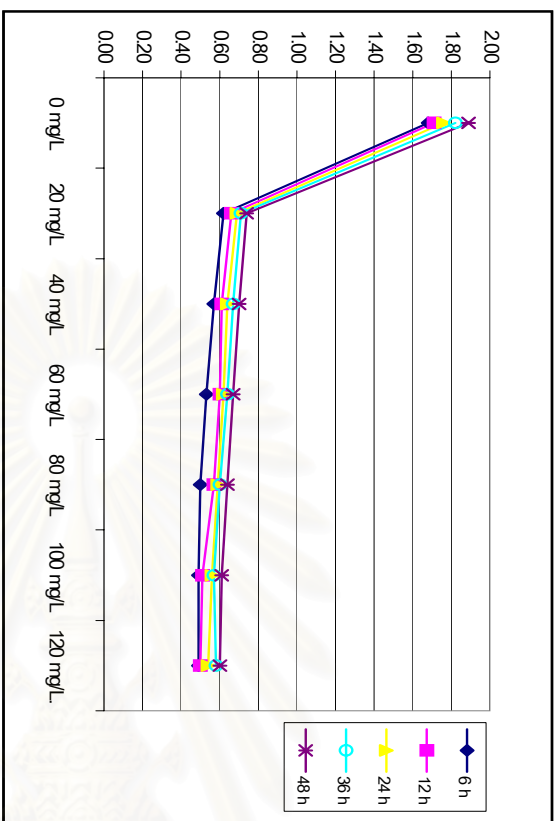
4-42 b Total insoluble of diesel fuel added with additive F after oxidation at 45 ° C



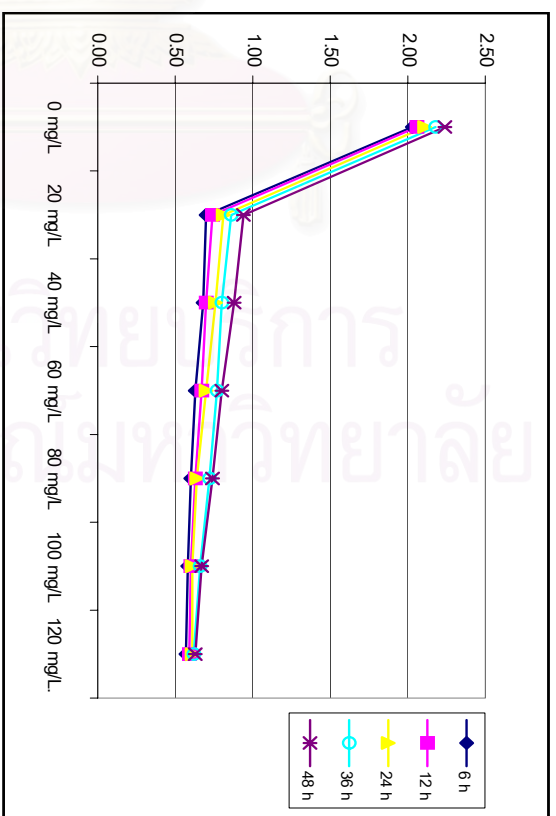
4-42 c Total insoluble of diesel fuel added with additive F after oxidation at 65 ° C



4-42 d Total insoluble of diesel fuel added with additive F after oxidation at 85 ° C



4-42 e Total insoluble of diesel fuel added with additive F after oxidation at 95 ° C



4-42 f Total insoluble of diesel fuel added with additive F after oxidation at 100 ° C

Figure 4-42 Total insoluble of diesel fuel added with the additive F after oxidation at various reaction times

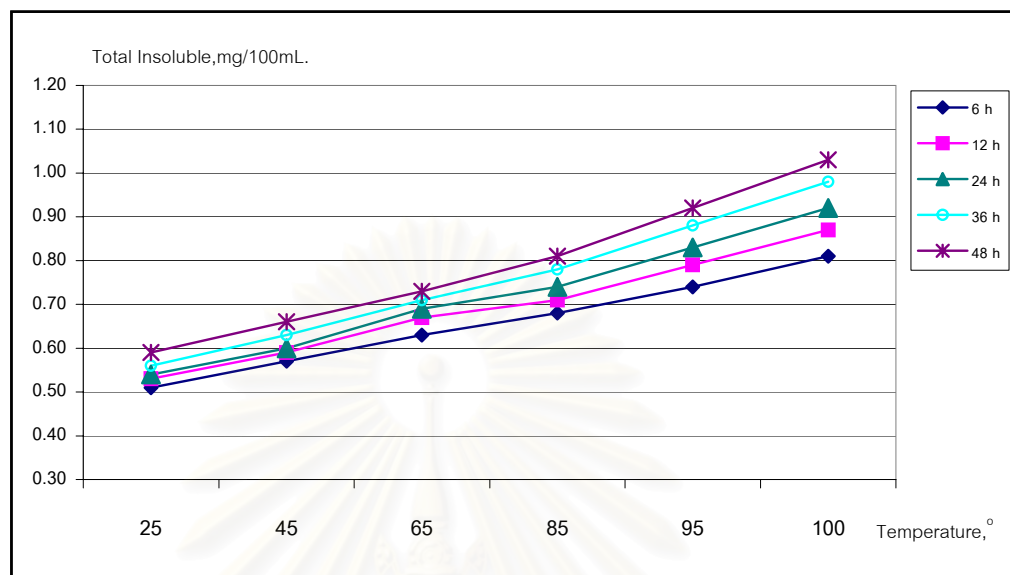


Figure 4-43 Total insoluble of diesel fuel blended with unknown additives after oxidation at various temperatures (varying in the reaction time)

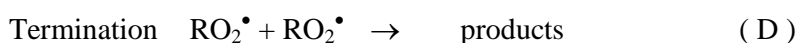
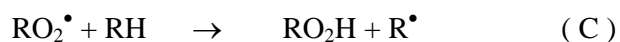
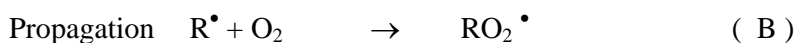
All of the results showed that reaction time, temperature and concentration of antioxidant additive have very significant influential on the increasing of total insoluble formation. These results showed that total insoluble was dependent on reaction time. All of figures in section 4.6.5, showed the relationship between the total insoluble content and reaction time in which the total insoluble increased at longer reaction time and high temperature. It was clear that the presence of a high concentration of antioxidant additives could reduce insoluble material occurred during oxidation. For example, the presence of 120 mg /l of additive F resulted in more than 50 % reduction in deposit formation with O₂ saturated sample after oxidation at 100 °C. Additionally, the presence of antioxidant additives seemed to delay the deposit formation in diesel fuel. However, additive B, which was a

phenol type antioxidant could reduce deposition until it was consumed. Then, the deposit formation continued rapidly. These data were indication of the efficiency of each antioxidant additive for delaying of deposition in the order of additive $F > A > D > E > B > C$. When compared the efficiency of antioxidant additive with unknown additive, it was found that additive E had more slightly effective than unknown additive. These results also indicated that antioxidant additive which acted as a dispersant or comprising of dispersant was predominant on reducing of total insoluble formation. It could prevent deposition by surrounding polar species and preventing them from agglomerating and / or reacting to form larger species that ultimately produce deposits.

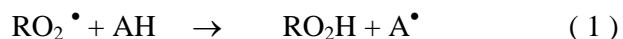
4.7 Evaluation of antioxidants behavior on improving diesel fuel stability.

The results in 4.6.1 could support the hypothesis that antioxidant additive can improve the diesel fuel stability by acting in two ways: 1. suppressing the normal radical propagation process by reacting with peroxy or alkyl radical as following in chain transfer reactions.

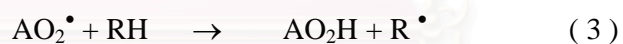
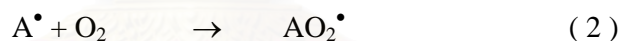
First, we explained these action by chain breaking mechanism of autoxidation reaction in chapter 2, starting with the basic chemistry of autoxidation chain reaction;



Whereas AH was a representative of antioxidant additive and is added into fuel. A chain-breaking antioxidant (AH) could add into this chain mechanism.



The antioxidant operates by transfer reaction (1), thus removing the chain carrying radical RO_2^\bullet , from the autoxidation process. To be effective, the new radical formed, A^\bullet , must not propagate the chain. This is easily accomplished if reaction (1) is significantly exothermic, implying that the AH bond strength is weak compared with RH, this prevents A^\bullet from regenerating the R^\bullet radical and continuing the chain. However, it is also possible that some of the A^\bullet radicals could combine with oxygen producing AO_2^\bullet peroxy radical as in reaction (2). In this case, reaction (3) must progress very slowly so that the chain propagation of autoxidation chain reaction (B) and (C), is effectively terminate by reaction(1)



It is generally argued that the activation energy for hydrogen atom abstraction by peroxy radicals as in reaction (3) depend on the carbon –hydrogen bond strength in RH , and not on the stability of the underlying radical of the peroxy radical A^\bullet . This would seem to indicate that the activation energy of reaction (3) is not significantly different from that of reaction C , and therefore the radical formed in reaction (2) would then be capable of regenerating the original chain.

There are three possible reasons for reaction (3) to be significantly slower than reaction (B). Firstly, there is steric hindrance which would lower the pre-exponential factor for the reaction. Secondly, as postulated here, is that there is stabilization across the O – O bond for some radicals and that the activation energy is increased. Thirdly, there may be a unimolecular rearrangement of the AO_2^\bullet radical after formation. It is of course possible that the A^\bullet radicals do not add oxygen.

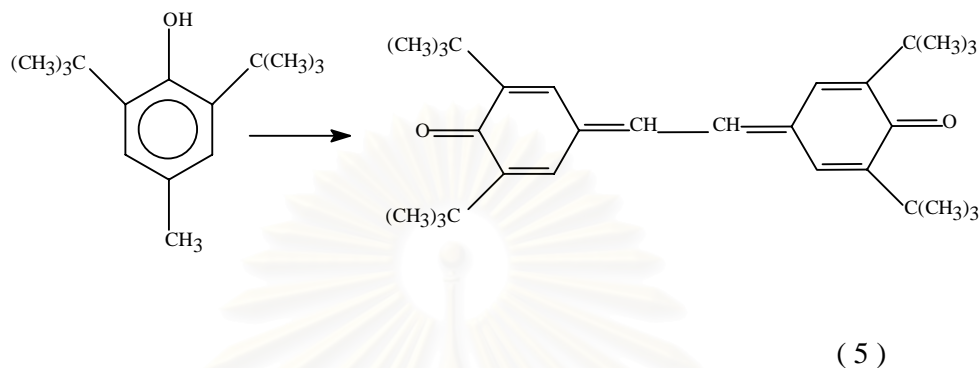
The radicals formed in reaction (1) or (2) are then consumed in the major termination reaction (4).

For this theory, one can propose that the major termination reaction is the major production pathway for total insoluble formation.

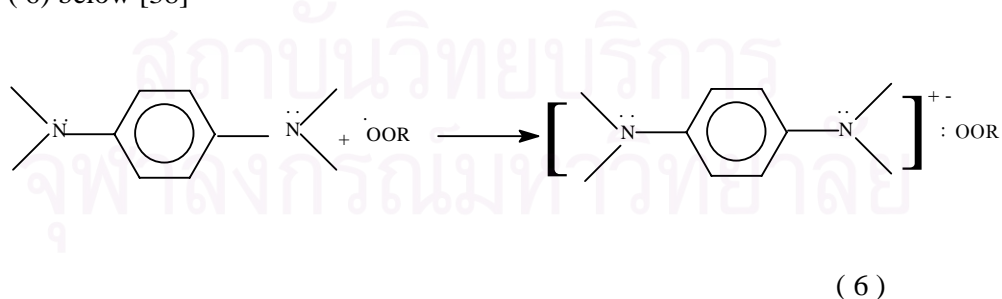
From equation above, we can say that antioxidant additive play a role of breaking the chain mechanism by intercepting the alkylperoxy radical, RO_2^\bullet [19].

The different behavior of each antioxidant type explained that the ability of antioxidant additive in delaying oxidation of diesel fuel was determined by different mechanism in the termination step. In theory, molecule of phenol type antioxidant could disable two peroxy radicals and could transform into phenoquinone compound by chemical oxidation [37]. So this antioxidant type could delay oxidation but had no net or slightly increase in peroxide species occurred during inhibition (see figure 4-22). In consistency with phenol type antioxidant consumption, the induction period over inhibited and accelerated regions was slowed with increasing antioxidant concentration. The termination

step in oxidation was shown in equation (5).



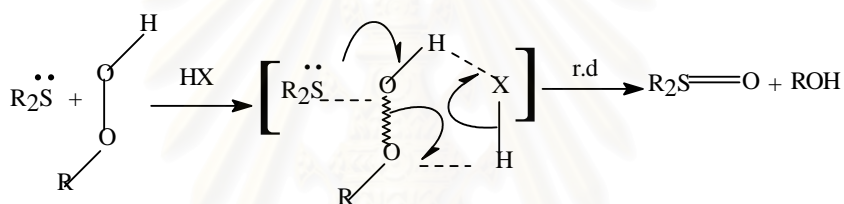
For amine type antioxidant had labile hydrogen atom, even complete N-alkylation of aromatic amines did not destroy their antioxidant character. In the absence of labile hydrogen atoms, the deactivating mechanism could involve electron transfer from nitrogen to form complexes with peroxy radical. Electron-donating group on the nitrogen decreased the ionization potential. Amine type antioxidants (*p*-phenylenediamine) are readily oxidized by free radicals or free radical sources to give radical cations called Wurster salts was shown in equation (6) below [38]



Therefore amine type antioxidant could increase the induction period, reduce PV and total insoluble formation. It also could reduce color development, because Wurster salts which was oxidation product, could dissolve in diesel fuel.

It was clear that these two primary antioxidant types retarded the oxidation reaction either with different efficiencies or by different mechanism.

For natural antioxidant presence in diesel fuel operated to reduce self-initiation by destroy ROOH. The autoxidation profiles unlike these two antioxidant types, did not exhibit the characteristic early initiation and followed by rapid autoxidation. For example, sulfides, thiophene were oxidized easily with alkyl hydroperoxides according to the mechanism as following below [6,39].



(7)

In general, the greatest benefit from natural inhibitors was realized during the time interval associated with rapid autoxidation. This was attributed to a reduction in self- initiation or autocatalysis resulting from ROOH destruction. It was clear that these benefits would be less important under low temperature condition where homolytic dissociation was significant. On the other hands at higher temperatures or other induced dissociation of ROOH was significant, the benefits of natural antioxidants can be very important (see figure 4-6).

Another way of dispersing sediment agglomerates to prevent filter blocking could reduce the amount of total insoluble. Conventional antioxidants

tended to be less effective in controlling color, therefore screening tests were needed to identify the most appropriate additive to control color development.

Results also indicated that metal deactivator additive was sometimes used in conjunction with stability improvers to prevent oxidation reactions or reduced oxidation catalysis from being catalyzed by heavy metal ions, particularly of copper, which presented in trace amounts in the fuel. This implied that MDA eliminated the source of metal ion-catalyzed free radical initiation by chelation of dissolved metal and preventing its interaction with ROOH [4]. In addition to its role as a chelant, MDA acted as a metal surface deactivator or as an antioxidant because the compound with an easily extractable hydrogen atom had antioxidant properties, and the MDA molecule had two easily abstractable phenolic hydrogen atoms.

For the effects of dispersant additives, the results could explain that the additives which were known as dispersant containing polar groups, were considered to function by mechanisms which include:

1. Surface action due to the polar group promoting the formation of a barrier film on critical surfaces.
2. Dispersant action due to the polymeric additives preventing agglomeration of particulate matter and keeping it dispersed.
3. Solvent action due to additives dissolving pre – formed deposits.

Surface action and dispersant action are the principal importance to the preventive or keep-clean function of detergents. Solvent action is of much more important in the removal of existing deposits or cleanup function [40].

4.8 Study of the optimum dosage of antioxidant additive for use

The results in 4.6.2 showed that antioxidants could slow oxidation (increase induction period and/or reduce peroxide value), which led to the reduction of total insoluble content and to reduce color development depended on the dosage which was used to improve fuel stability. Clearly, diesel fuel containing high concentration of antioxidant additives had the stability enhanced. Although the appropriate dosage depended upon how long the storage period was in a specific field situation, but in this case study it suggested that for 1 year storage at the normal storage condition (temperature does not over than 45°C), the optimum dosage was recommended at about 40-60 mg/l.

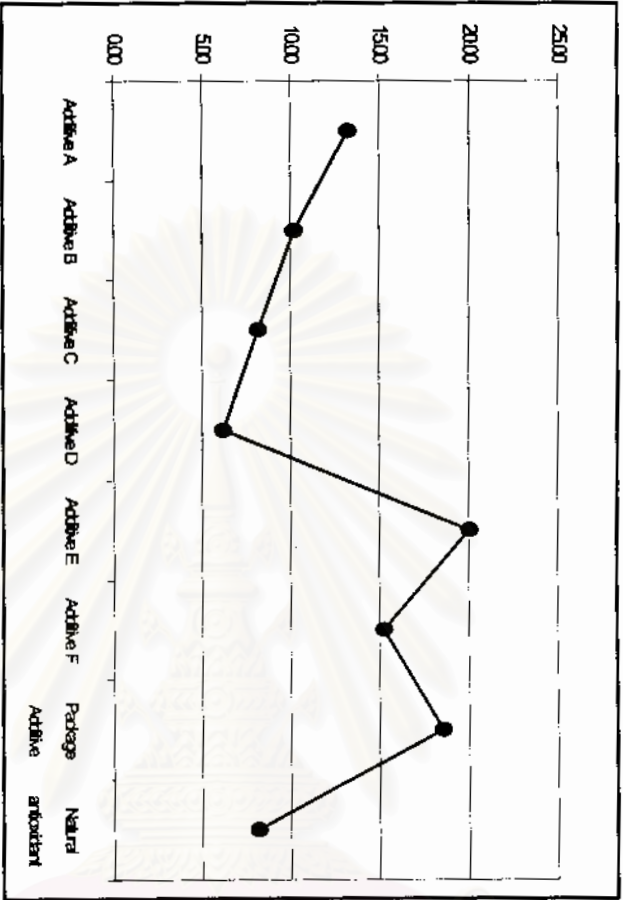
4.9 The impacts of the combination of additives on the stability of diesel fuel

Sample D was chosen for additional study because it was a typical diesel fuel which was composed of heavy gas oil, light gas oil and hydrocracking gas oil, approximately in the ratio of 65:10:25. This ratio was a representative of diesel fuel finished form for sale. The samples were blended with combination of additives which prepared from three types of antioxidant additives which were amine type, metal deactivator and dispersant additive in ratio 1: 1: 1. All samples were investigated by oxidation in oxidation bath at the controlled temperature at 95 ° C. The results were compared with single antioxidant additive (additives A-D) and natural antioxidant (sulfur and nitrogen heteroatom which contained in

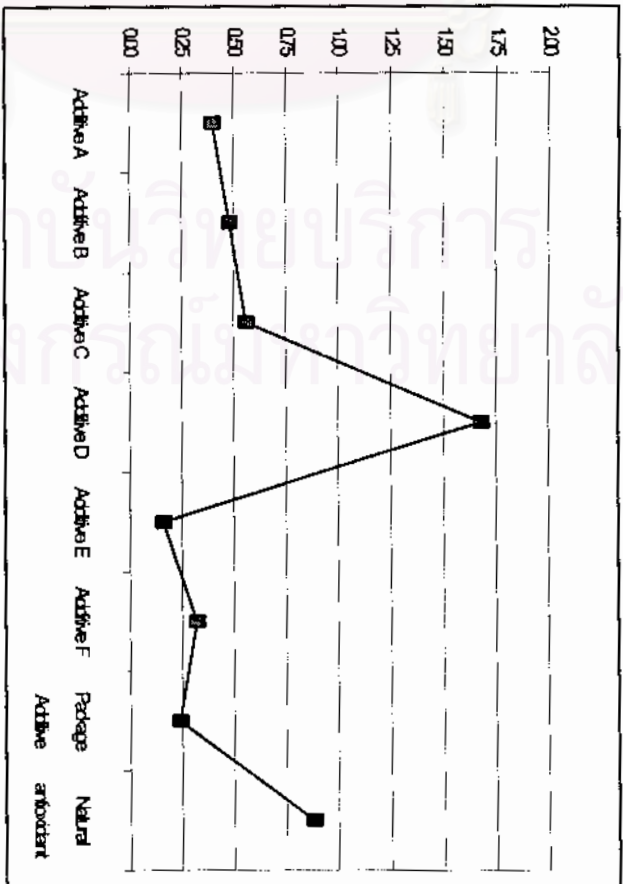
origin straight-run fuel). The impacts of combination additive on the stability of diesel fuel were shown in the figures below.



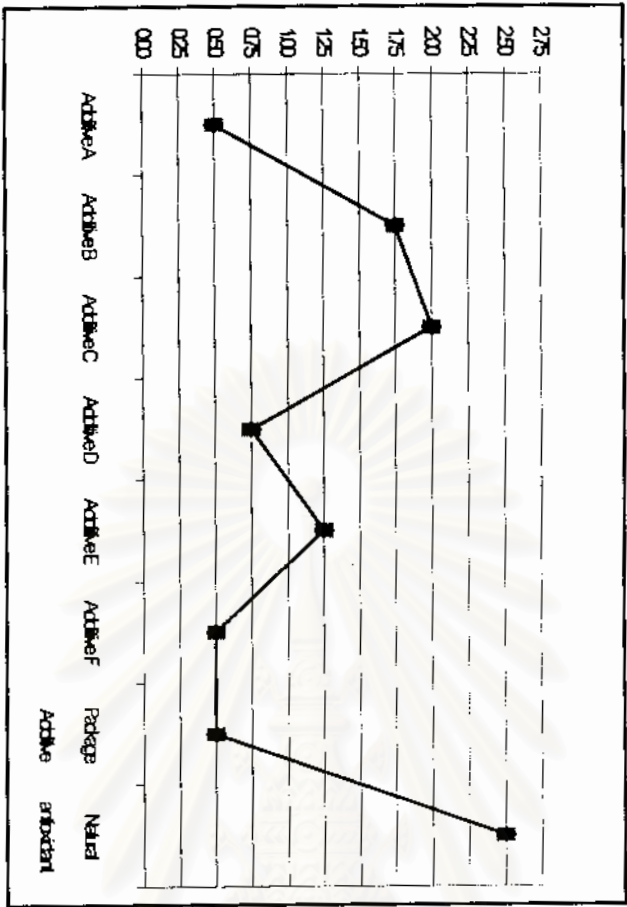
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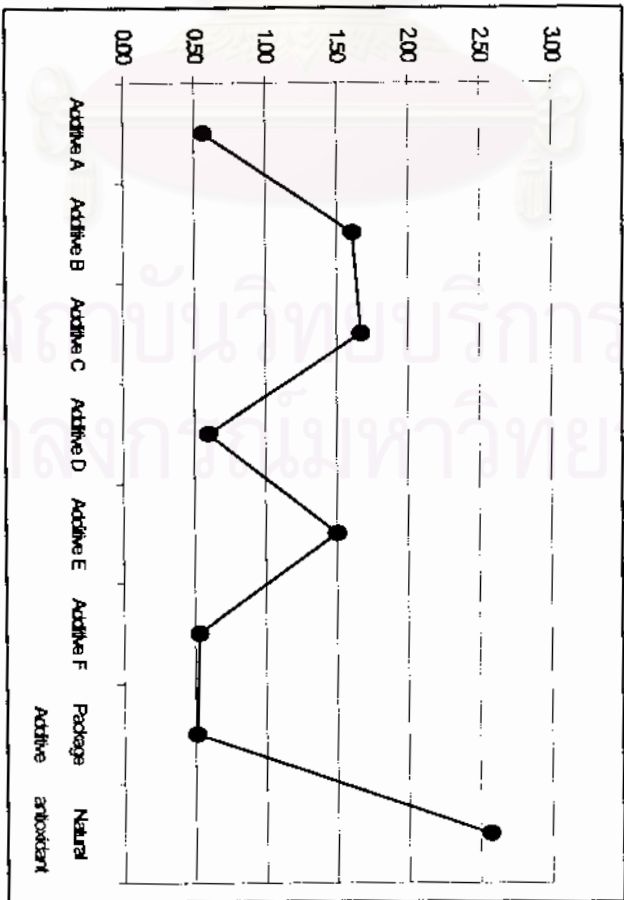
4-44 a Induction period after oxidation at 95 ° C, h



4-44 b Peroxide value after oxidation at 95 ° C, mg/kg



4-44 c ASTM Color after oxidation at 95 ° C



4-44 d Total insoluble after oxidation at 95 ° C, mg/100 ml

Figure 4-44 The impact of combination additive on the stability of diesel fuel after oxidation at 95°C

The results showed that the combination of additives which contained antioxidant, metal deactivator and dispersant had recently been shown to be more effective than single additive in slowing autoxidation (both could increase induction period and reduce peroxide value). It could reduce insoluble formation and color development. Each additive which comprising in the combined additive operated by distinctly different mechanism to have synergistic benefits. Those operating by similar mechanism had benefits accrued when used in combination of additives. A fixed concentration of each additive was chosen for investigation of the impact of these antioxidants in combination. The effect in figure 4 – 44(a) to 4-44 (d) of the package additive, demonstrated that it was better efficiency than either individual component. The effect in this figure also indicated that the combination additive was more effective than the natural inhibitor alone. All of results showed that the additive package combined the separate actions of antioxidant and metal deactivator could slow oxidation and dispersant additive could prevent deposition. The observed effect from this combination was approximately equal to the sum of the individual effects.

4.10 Further studies of the impacts of antioxidant additives to improve diesel fuel stability at different storage conditions

The effects of the storage condition on the stability of diesel fuel was studied by keeping the tested samples in the dark to avoid light, at in ambient temperature which was controlled at 22 ± 3 ° C and outdoor which had no temperature controlled. All samples were kept for one month. The effects of

storage conditions were characterized by color development and total insoluble formation in fuels after one month. This studied also investigated the stability of diesel fuel by varying in percentage of hydrocracking gas oil fraction. Finally the impacts of antioxidant additives on the stability of diesel fuel at each storage condition was investigated by blended sample with selected antioxidant. The results of effects of the storage condition were shown in the figures 4-45 to 4-52 below.

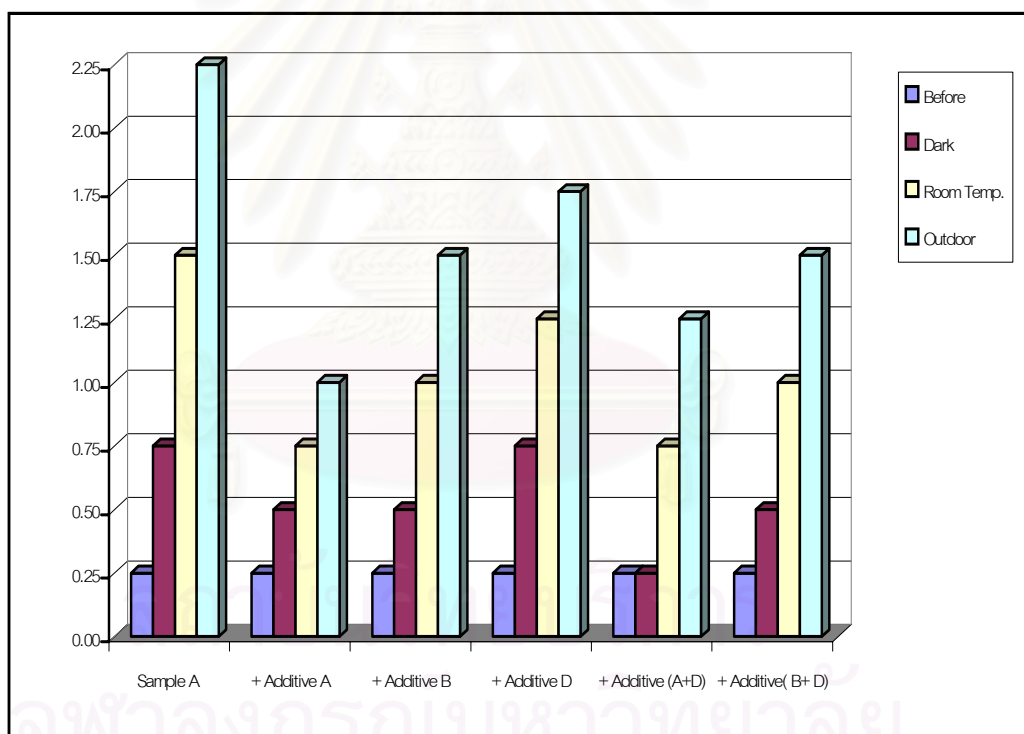


Figure 4-45 ASTM Color of heavy gas oil at different storage conditions for 1 month

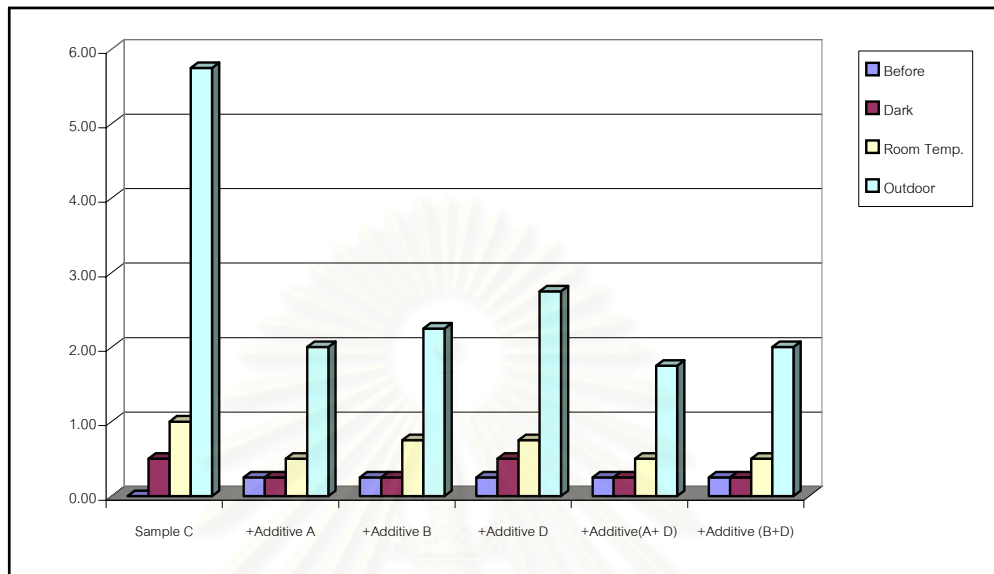


Figure 4-46 ASTM Color of hydrocracking gas oil at different storage conditions for 1 month

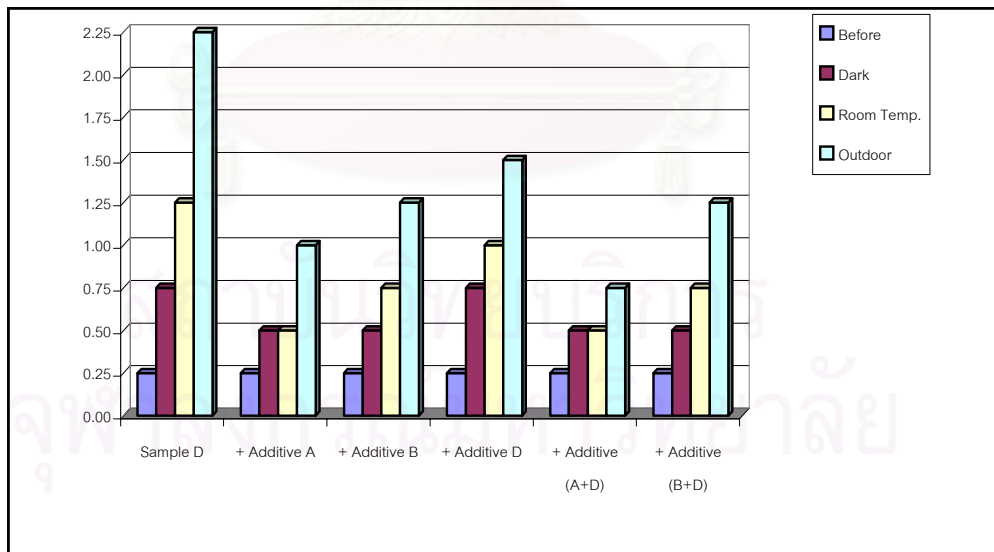


Figure 4-47 ASTM Color of diesel fuel at different storage conditions for 1 month

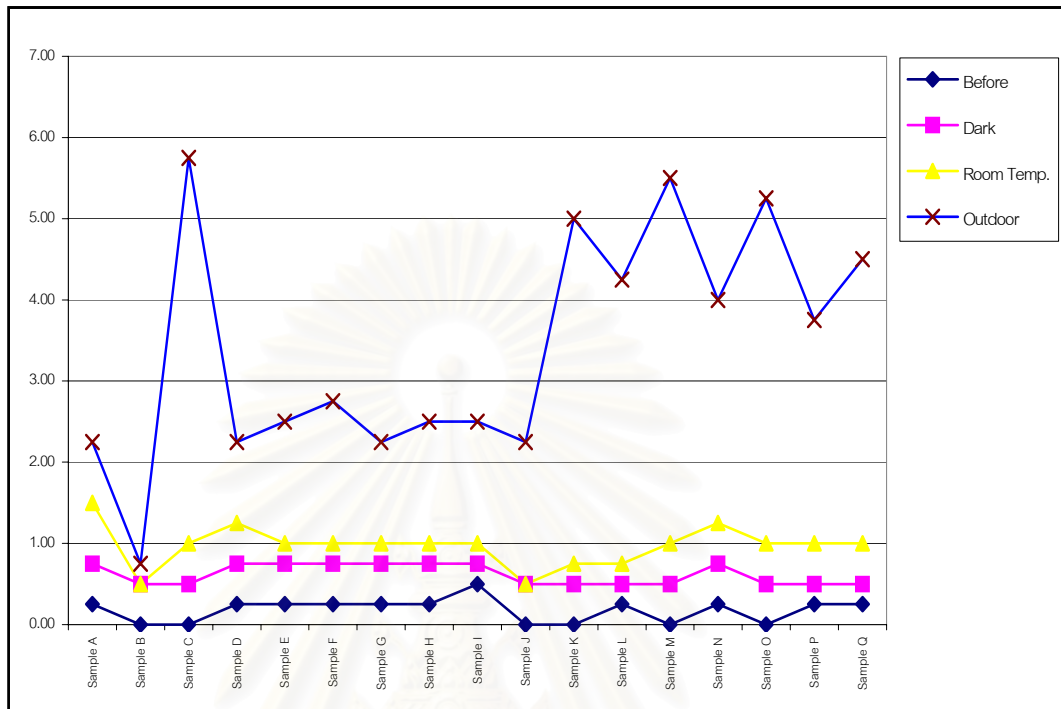


Figure 4-48 ASTM Color of diesel fuel at different storage conditions for 1 month (varying in % of hydrocracked gas oil fraction)

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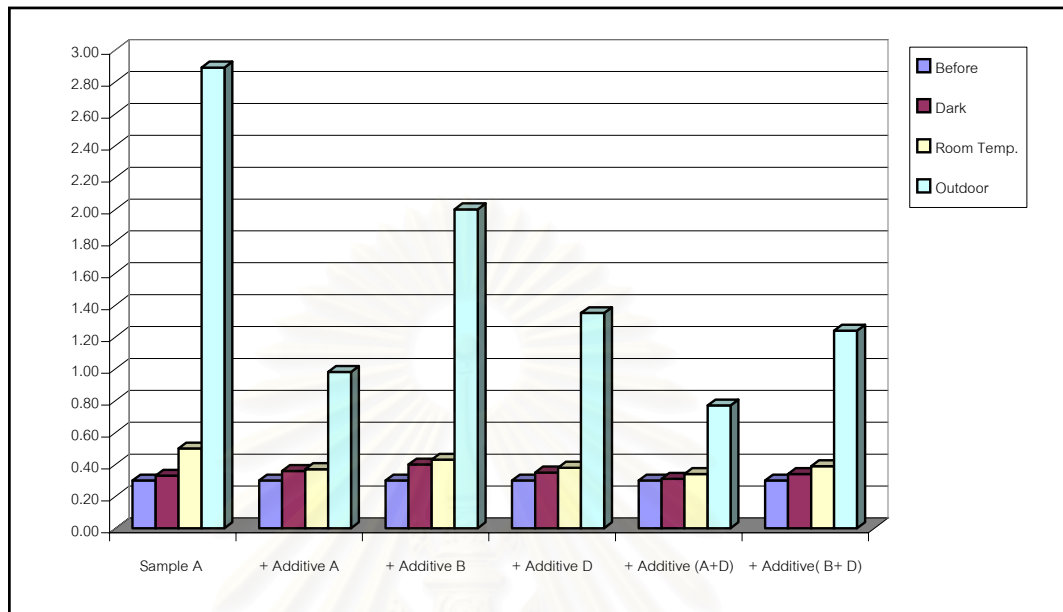


Figure 4-49 Total insoluble of heavy gas oil at different storage conditions for 1 month

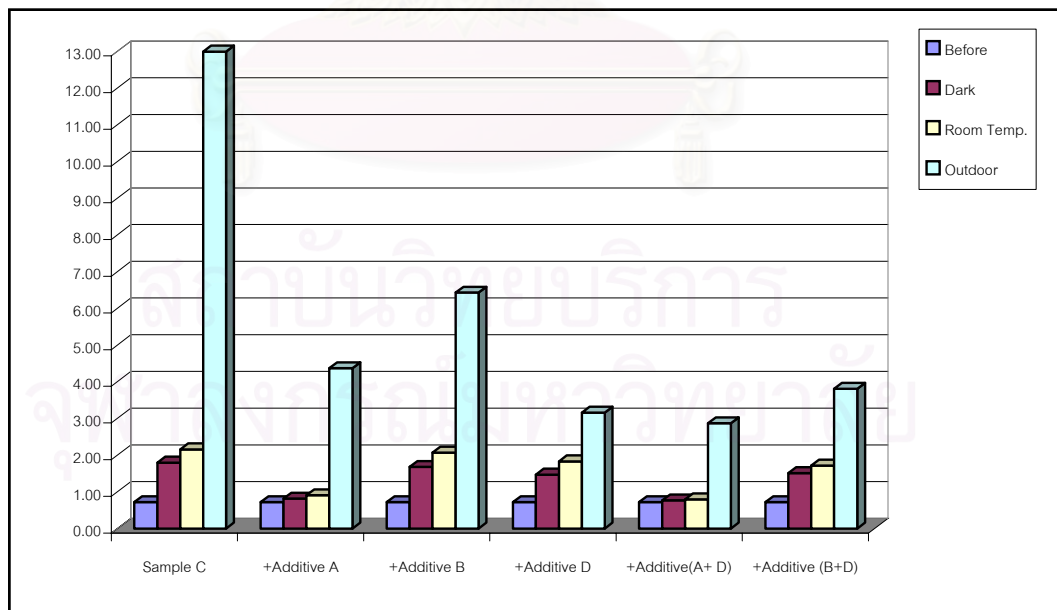


Figure 4-50 Total insoluble of hydrocracking gas oil at different storage conditions for 1 month

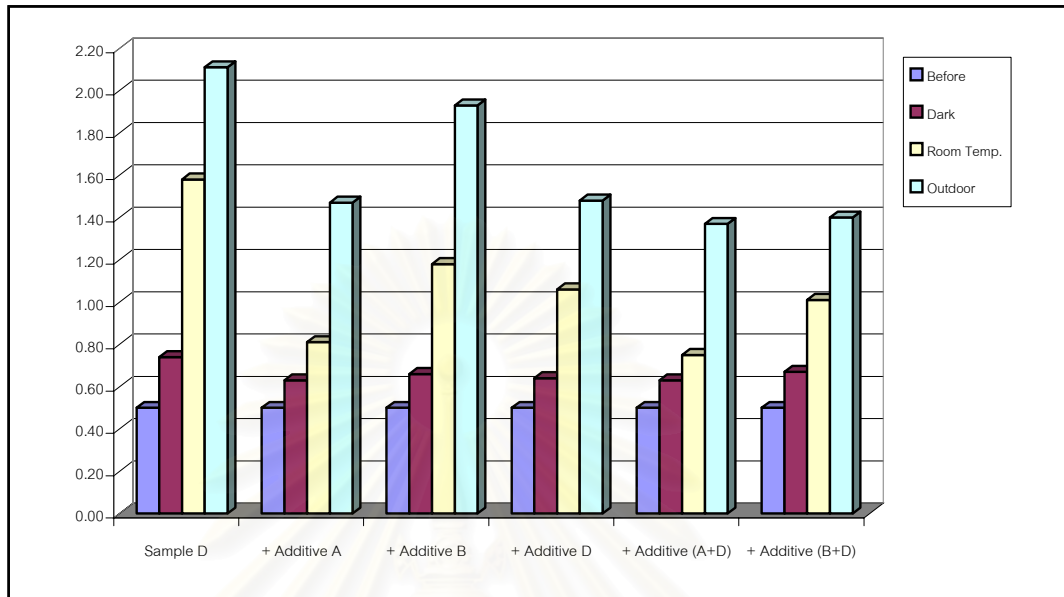


Figure 4-51 Total insoluble of diesel fuel at different storage conditions for 1 month

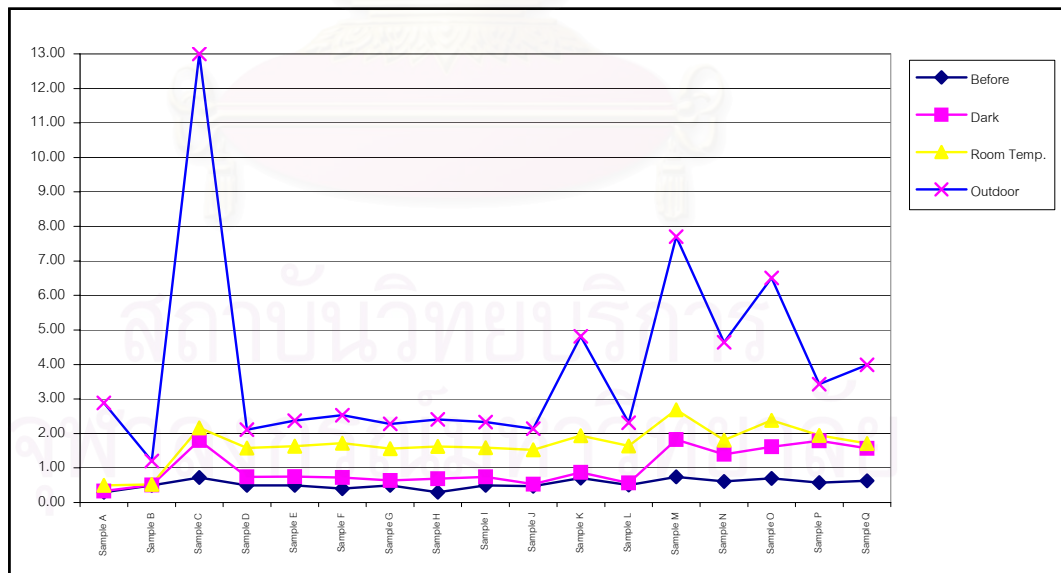


Figure 4-52 Total insoluble of diesel fuel at different storage conditions for 1 month (varying in % of hydrocracked gas oil fraction)

All of the results demonstrated that color development and deposit formation (or total insoluble occurring) were formed in diesel fuels during extended storage. The stability properties of diesel fuel were highly dependent on the composition of the distilled fuels such as heavy gas oil, light gas oil and hydrocracking gas oil. Figure 4-48 and 4-52 showed that the stability of diesel fuel at each storage conditions was inversely correlated with the percentage of hydrocracking gas oil that comprising in diesel fuels. For example, diesel fuel which having 100 % of hydrocracking gas oil (sample C) which was kept outdoor and had no temperature controlled and did not keep out of light had the most fuel instability. In this fuel, ASTM Color increased from 0 to 5.75 and the total insoluble increased from 0.72 to 13.00 mg/100 ml. Sample B which was a diesel fuel having 100 % of light gas oil fraction was the most stable fuels. It gave the least color development and deposit formation. While sample A had a moderate increasing of insoluble formation and color development.

The results in all figures indicated that sunlight or light was directly influence on diesel fuel towards instability. It accelerated oxidation of fuel to form insoluble products and developed color until darker than specification required. However, antioxidants could improve fuels stability by inhibiting oxidation, reduce total insoluble formation and controlled color development in fuel at each storage condition. For the samples which were kept outdoor, found that 100 mg/l of additive A could reduced total insoluble content from 2.89 to 0.98 in sample A, from 13.0 to 4.37 mg/100 ml in sample C and from 2.11 to 1.47 mg/100 ml in sample D, respectively. These data indicated that the chemical precursors which

responsible for instability of diesel fuel were predominantly in hydrocracking gas oil. Therefore diesel fuel which having high levels of hydrocracked gas oil fraction required suitable synthetic antioxidant to limit autoxidation during extended storage. Moreover it could also slow down autoxidation from light catalyzed reaction. Although antioxidants which were used in this case could improve the stability of diesel fuel by reducing the amount of total insoluble and color development, but these antioxidants tended to be less effective in controlling sediment formation.

From the results in figure 4-45, 4-46,4-47, 4-49,4-50 and 4-51, it indicated that dispersant (Additive D) could contribute to the reduction of total insoluble formation and color development. The impacts of the additive combination (A+D) that was a combination of an amine type antioxidant with additive D that acted as dispersant was greater in the reduction of total insoluble than the combination of additive(B+D) which was a phenol type antioxidant combined with additive D. Both combination additives had been shown to be more effective than individual additive.

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CHAPTER V

CONCLUSION AND SUGGESTION

According to the studies of the effects of antioxidants on the stability of diesel fuel, it indicated that the stability was characterized in term of the induction period , peroxide value, total insoluble and color development. There were four significant factors which led to diesel fuel instability. They were;

1. The percentage of hydrocracked gas oil fraction which comprising in the blends of diesel fuel.
2. N,S-heteroatom containing in diesel fuels that acted as a natural antioxidant
3. Temperature
4. The storage conditions of diesel fuel.

The antioxidant additive behavior was evaluated based on the ability in delaying the oxidation rate and to reduce deposition and color development. Moreover this investigation also made understand the total insoluble formation and oxidation mechanism in diesel fuel.

From studies of the effects of antioxidants on the stability of diesel fuel, we found that antioxidants could improve fuel stability from degradation to meet specification requirement. They were very effective in the increasing of induction period, while decreasing of peroxide value, total insoluble and color development in diesel fuel. The antioxidant can be used to slow oxidation by suppressing the normal radical propagation process by reacting with peroxy or alkyl radical in

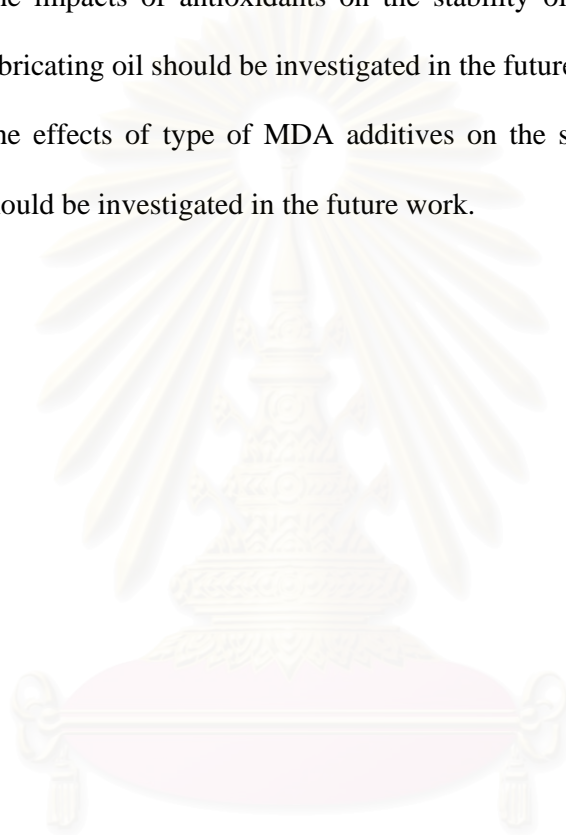
chain transfer and was dispersing sediment agglomerates or reacting to form larger species that ultimately produce deposits. However different antioxidant type retarded oxidation by different mechanism. The results also indicated that amine type antioxidant was more effective than phenol type antioxidant at the same concentration. Antioxidants were very effective in improving fuel stability when was concentration increasing. They could mainly control the tendency of diesel fuel which having high levels of hydrocracking gas oil fraction towards the formation of insoluble products and much more color developed, but they were ineffective or less effective in diesel fuel with high concentration of N, S-heteroatom.

The studies of the optimum dosage of antioxidant additives for use, we suggested that for 1 year storage at normal storage condition (temperature not over than 45 °C), the optimum dose was about 40–60 mg/l. Additionally, the synergistic benefit to improve stability, could be achieved by the combination of additives.

Further studies on the impacts of antioxidant additive for improving diesel fuel stability at each storage condition concluded that suitable antioxidant needed to limit autoxidation in diesel fuel with high levels of hydrocracked gas oil fraction (more than 25 %) and lacking of natural antioxidant. For diesel fuel which having high levels of aromatic compound and could not keep out of light, the combination of amine type and dispersant additive was suitable. Moreover antioxidants needed to limit fuel degradation during long term storage.

SUGGESTION

1. The effects of type of sulfur compound on the stability of diesel fuel should be investigated in the future work.
2. The impacts of antioxidants on the stability of Jet A-1, gasoline or lubricating oil should be investigated in the future work.
3. The effects of type of MDA additives on the stability of diesel fuel should be investigated in the future work.



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APPENDIX A

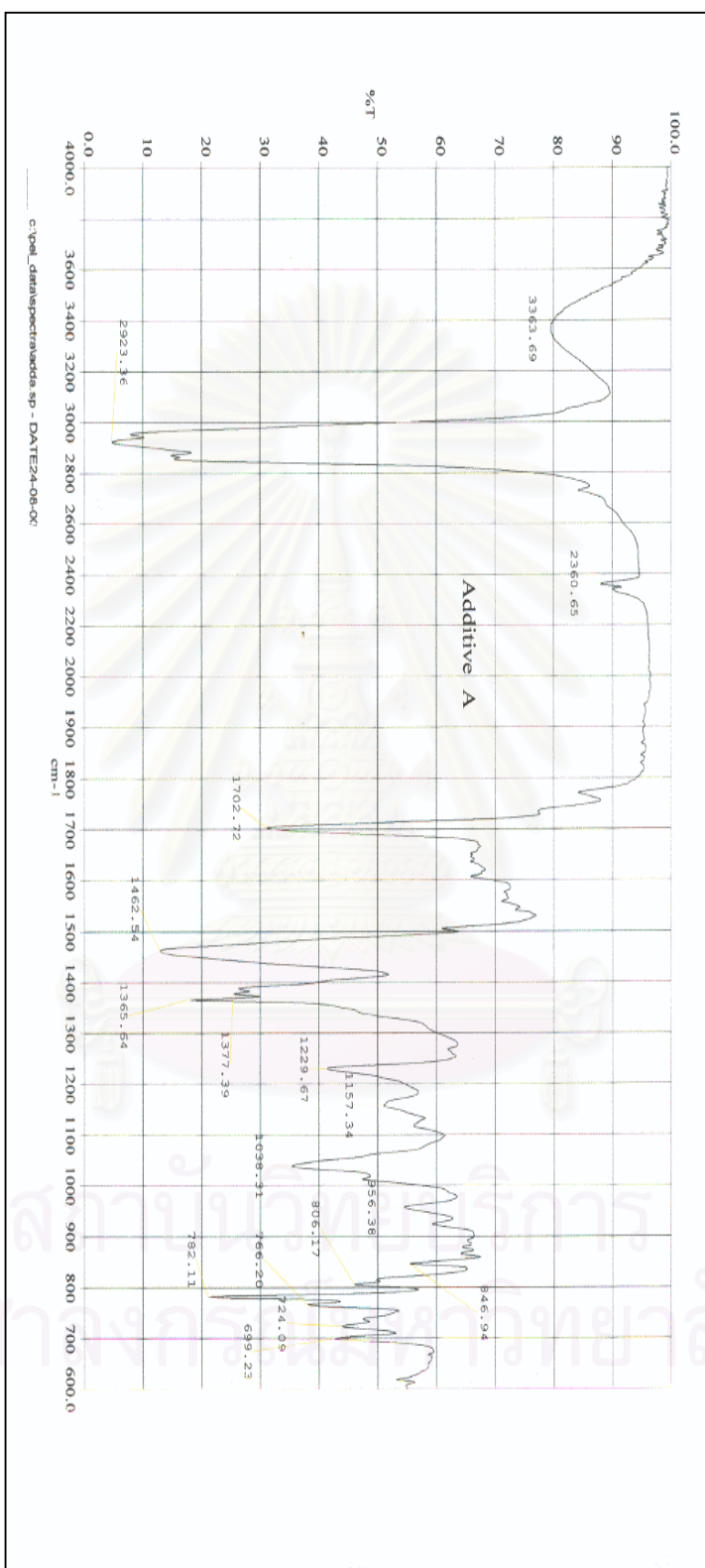


Figure A1 The FT-IR spectrum band of additive A

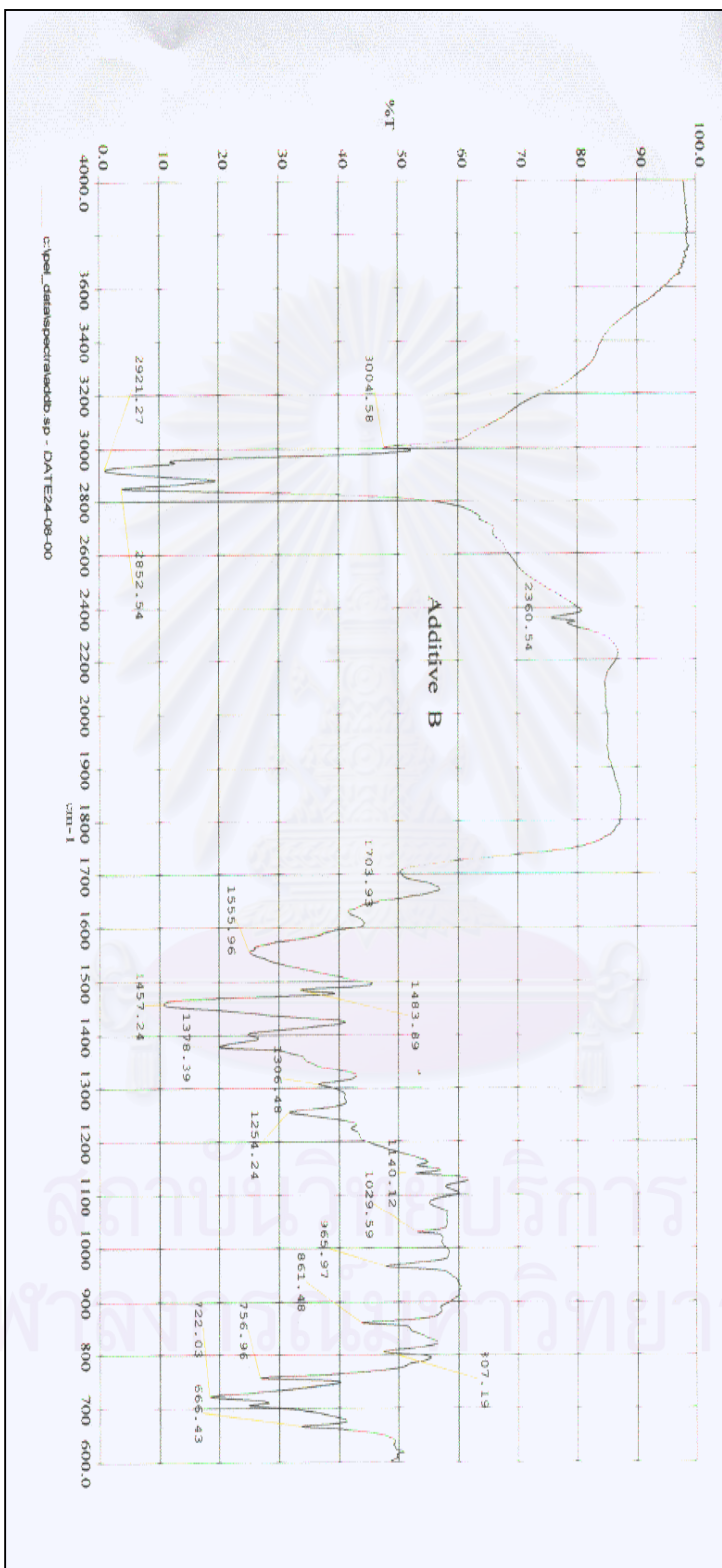


Figure A2 The FT-IR spectrum band of additive B

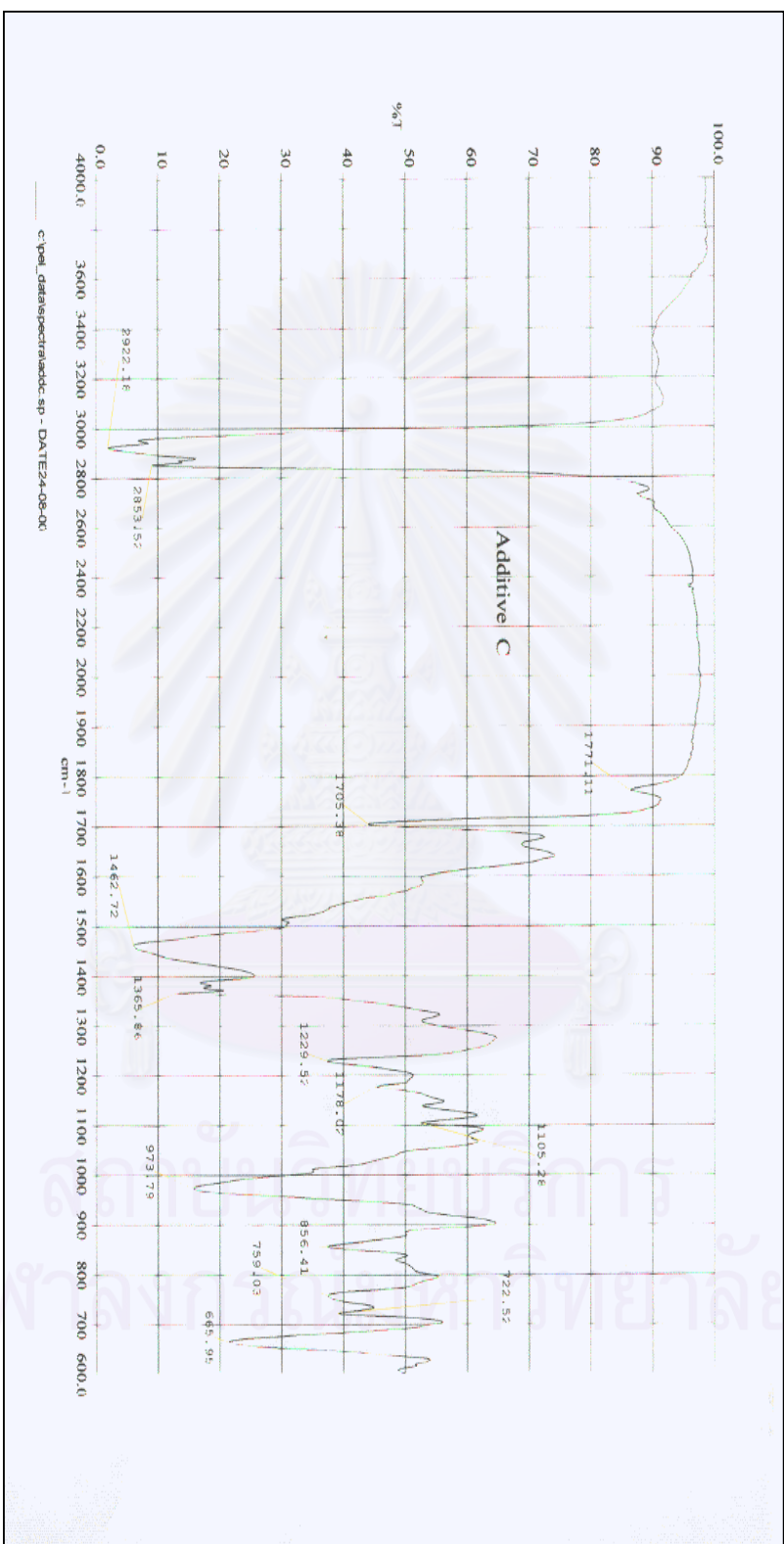


Figure A3 The FT-IR spectrum band of additive C

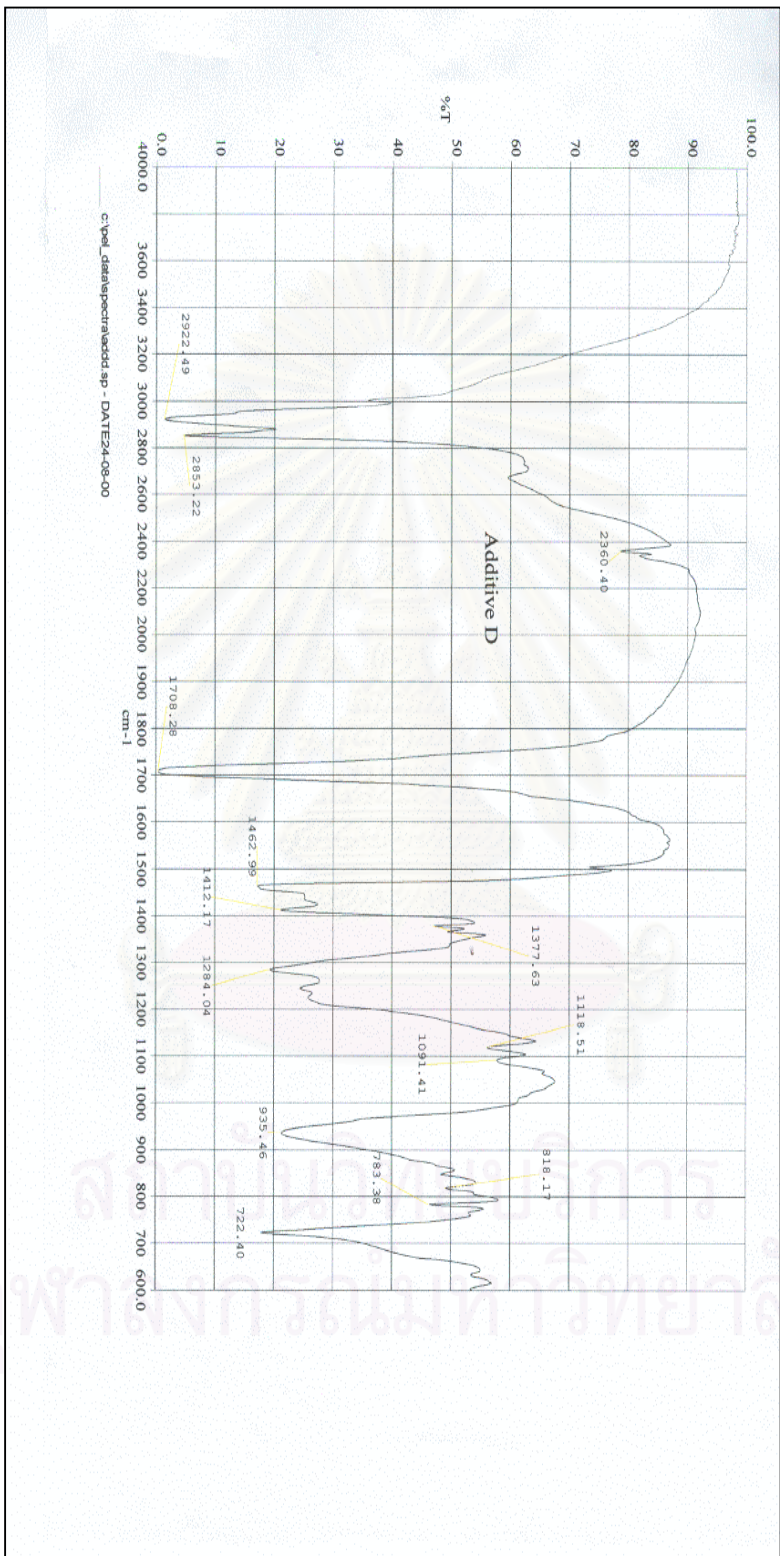


Figure A4 The FT-IR spectrum band of additive D

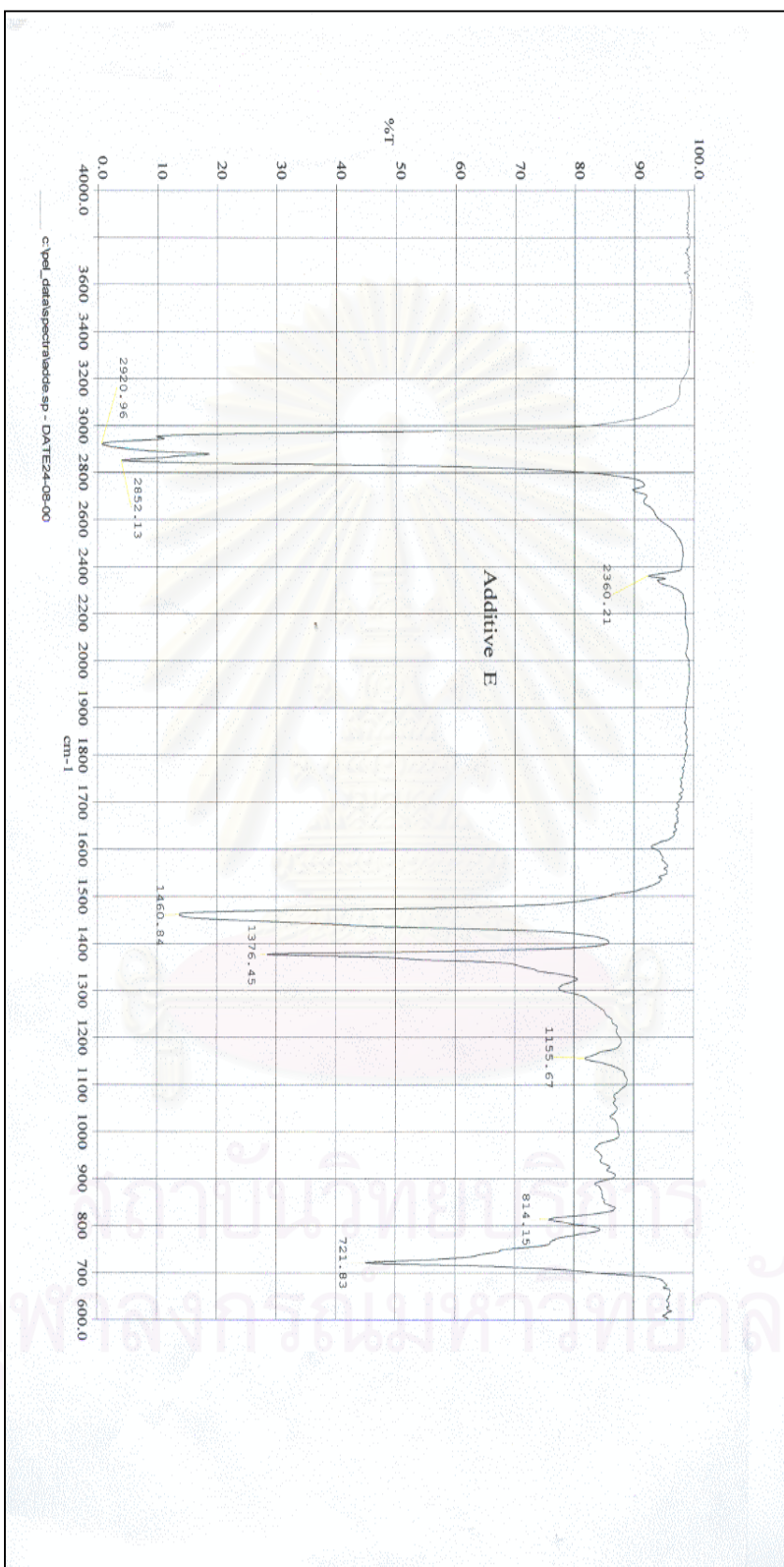


Figure A5 The FT-IR spectrum band of additive E

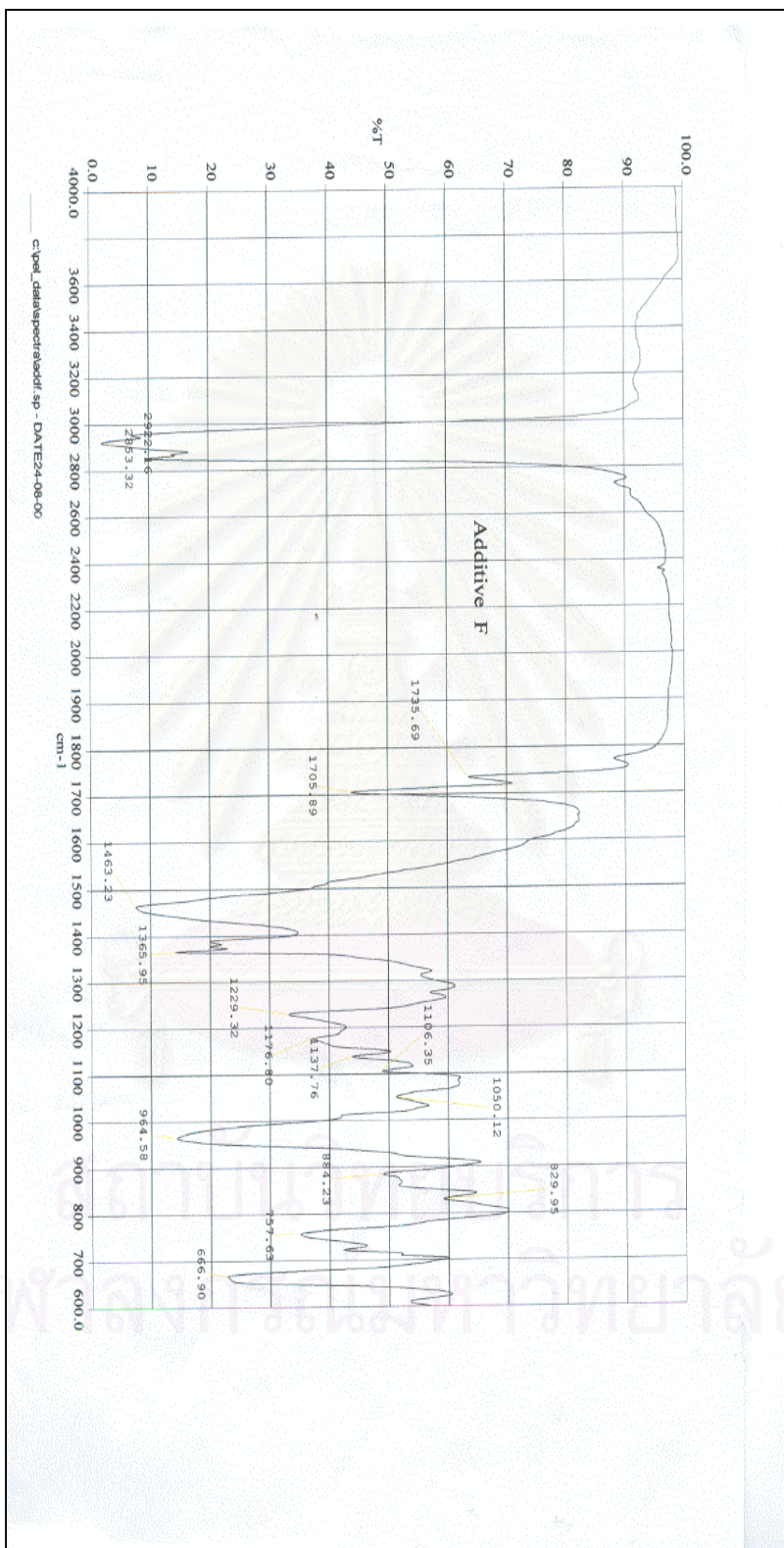


Figure A6 The FT-IR spectrum band of additive F

APPENDIX B

Study of the stability of diesel fuel before introducing of antioxidant additives

Table B1 Induction period of diesel fuel before introducing of antioxidant additives after oxidation at various temperatures.

Sample	Induction period after oxidation at various temperatures ,h					
	25 °C	45°C	65°C	85°C	95°C	100°C
A	21.45±0.21	18.47±0.18	12.36±0.31	10.49±0.10	8.18±0.08	6.42±0.13
B	20.48±0.23	17.26±0.17	10.31±0.10	8.52±0.08	7.41±0.10	5.17±0.12
C	16.00±0.17	12.27±0.12	6.30±0.06	4.30±0.23	3.33±0.20	2.34±0.16
D	18.30±0.18	16.36±0.16	9.49±0.09	7.31±0.07	5.58±0.10	4.37±0.23
I	20.46±0.20	17.30±0.17	12.00±0.12	10.00±0.10	7.45±0.14	5.50±0.11

Table B2 Peroxide value (PV) of diesel fuel before introducing of antioxidant additives after oxidation at various temperatures.

Sample	Peroxide value(PV) after oxidation at various temperatures ,mg /kg.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
A	1.20±0.08	1.12±0.05	0.64±0.03	0.72±0.03	0.80±0.03	0.88±0.03	0.96±0.05
B	1.20±0.08	1.20±0.08	1.28±0.05	1.36±0.08	1.44±0.05	1.52±0.05	1.52±0.03
C	1.44±0.08	1.52±0.08	1.76±0.08	1.92±0.05	2.00±0.08	2.24±0.08	2.48±0.08
D	1.12±0.03	1.20±0.05	1.28±0.08	1.36±0.05	1.44±0.08	1.52±0.08	1.60±0.08
I	0.48±0.05	0.56±0.03	0.64±0.05	0.72±0.03	0.72±0.03	0.80±0.03	0.88±0.03

Table B3 Total insoluble of diesel fuel before introducing of antioxidant additives oxidation at various temperatures.

Sample	Total insoluble after oxidation at various temperatures ,mg/100 ml.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
A	0.30±0.01	0.30±0.02	0.69±0.04	0.96±0.07	2.11±0.18	2.57±0.21	2.68±0.26
B	0.50±0.03	0.51±0.01	0.60±0.03	0.71±0.05	1.11±0.09	1.35±0.13	1.65±0.13
C	0.70±0.04	0.72±0.04	0.84±0.06	0.90±0.08	1.27±0.11	1.83±0.18	2.06±0.20
D	0.50±0.02	0.52±0.06	0.66±0.03	0.73±0.04	1.24±0.14	1.57±0.15	1.65±0.16
I	0.50±0.01	0.51±0.03	0.54±0.02	0.62±0.04	0.63±0.05	0.66±0.06	0.68±0.07

Table B4 ASTM Color of diesel fuel before introducing of antioxidant additives after oxidation at various temperatures.

Sample	ASTM Color after oxidation at various temperatures						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
A	0.25	0.75	1.00	1.50	2.00	2.50	2.75
B	0	0.25	0.25	0.75	1.25	1.75	2.00
C	0	0.25	0.75	0.75	1.50	2.00	2.50
D	0.25	0.50	0.50	1.00	1.25	2.00	2.25
I	0.50	0.50	0.50	0.75	1.00	1.25	1.50

APPENDIX C

Study of the effects of sulfur content

Table C1 Induction period of hydrocracked gas oil after oxidation at various temperatures (varying in % of sulfur content)

Sulfur Content, in wt %	Induction period after oxidation at various temperatures ,h					
	25 °C	45°C	65°C	85°C	95°C	100°C
Neat Fuel	16.00±0.17	12.27±0.12	6.30±0.06	4.30±0.23	3.33±0.20	2.34±0.16
0.030	18.12±0.18	12.40±0.12	7.00±0.07	5.15±0.05	4.05±0.04	3.10±0.03
0.050	18.47±0.18	12.57±0.12	9.46±0.09	5.48±0.06	4.31±0.04	3.51±0.03
0.075	19.56±0.19	14.16±0.14	10.20±0.10	7.36±0.07	4.42±0.4	4.36±0.04
0.100	20.30±0.20	15.42±0.15	11.54±0.11	8.15±0.08	6.62±0.06	5.32±0.05
0.120	21.40±0.21	18.26±0.18	12.20±0.10	10.20±0.10	8.46±0.08	7.54±0.07

Table C2 Peroxide value(PV) of hydrocracked gas oil oxidation at various temperatures (varying in % of sulfur content)

Sulfur Content, in % wt	Peroxide value(PV) after oxidation at various temperatures, mg/kg						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
Neat Fuel	1.44±0.08	1.52±0.08	1.76±0.08	1.92±0.08	2.00±0.08	2.24±0.08	2.48±0.08
0.030	1.44±0.05	1.36±0.08	1.52±0.08	1.60±0.05	1.68±0.08	1.76±0.08	1.84±0.08
0.050	1.36±0.03	1.28±0.05	1.44±0.05	1.52±0.08	1.60±0.05	1.68±0.05	1.76±0.03
0.075	1.44±0.05	1.20±0.03	1.36±0.03	1.20±0.05	1.28±0.05	1.28±0.05	1.52±0.00
0.100	1.20±0.08	1.20±0.03	0.96±0.05	1.04±0.03	1.20±0.05	1.28±0.03	1.44±0.03
0.120	1.28±0.08	0.72±0.05	0.72±0.08	0.88±0.03	0.96±0.03	1.04±0.03	1.12±0.03

Table C3 Total Insoluble) of hydrocracked gas oil after oxidation at various temperatures (varying in % of sulfur content)

Sulfur Content, in wt %	Total insoluble after oxidation at various temperatures , mg/100 ml.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
Neat Fuel	0.70±0.04	0.72±0.04	0.84±0.06	0.90±0.08	1.27±0.11	1.83±0.18	2.06±0.20
0.030	0.70±0.07	0.72±0.03	0.86±0.08	0.95±0.03	1.29±0.29	1.84±0.11	2.09±0.20
0.050	0.70±0.05	0.71±0.02	0.85±0.06	0.98±0.08	1.33±0.13	1.86±0.20	2.11±0.12
0.075	0.71±0.08	0.72±0.06	0.86±0.05	0.98±0.05	1.34±0.10	1.87±0.19	2.22±0.22
0.100	0.71±0.05	0.72±0.08	0.87±0.04	1.03±0.11	1.36±0.12	1.99±0.20	2.29±0.23
0.120	0.71±0.05	0.73±0.07	0.87±0.07	1.07±0.13	1.41±0.14	2.00±0.20	2.41±0.24

Table C4 ASTM Color of hydrocracked gas oil after oxidation at various temperatures (varying in % of sulfur content)

Sulfur Content, in wt %	ASTM Color after oxidation at various temperatures						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
Neat Fuel	0	0.25	0.25	0.75	1.50	2.00	2.50
0.030	0.25	0.50	1.00	1.25	1.25	1.75	2.50
0.050	0.25	0.50	0.75	1.00	1.50	2.00	2.25
0.075	0.25	0.50	0.75	1.00	1.25	1.50	2.50
0.100	0.25	0.50	1.00	1.50	1.75	2.00	2.75
0.120	0.25	0.50	1.00	1.50	2.00	2.25	2.75

APPENDIX D

Study of the effects of N-heteroatom content

Table D1 Induction period of hydrocracked gas oil after oxidation at various temperatures (varying in % of nitrogen content)

Spiked sample with Pyridine	Induction period after oxidized at various temperatures ,h					
	25 °C	45°C	65°C	85°C	95°C	100°C
Neat Fuel (Sample C)	16.00±0.17	12.27±0.12	6.30±0.06	4.30±0.23	3.33±0.20	2.34±0.16
Sample C + 0.03% vol.	19.37±0.19	13.27±0.13	9.46±0.09	5.49±0.06	4.47±0.04	3.48±0.03
Sample C + 0.05% vol.	22.46±0.22	15.11±0.15	11.17±0.11	7.57±0.08	6.24±0.06	5.39±0.05
Sample C + 0.075% vol.	25.10±0.25	19.06±0.20	14.3±0.14	10.51±0.10	9.04±0.09	8.31±0.08
Sample C + 0.100% vol.	25.48±0.26	21.42±0.21	17.18±0.17	13.26±0.13	11.48±0.11	10.49±0.14
Sample C + 0.120% vol.	26.20±0.26	23.19±0.23	18.07±0.18	15.42±0.15	13.48±0.13	12.56±0.13

Table D2 Peroxide value (PV) of hydrocracked gas oil after oxidation at various temperatures (varying in % of nitrogen content)

Spiked sample with Pyridine	Peroxide value(PV) after oxidation at various temperatures ,mg/kg.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
Neat Fuel (Sample C)	1.44±0.08	1.52±0.08	1.76±0.08	1.92±0.08	2.00±0.08	2.24±0.08	2.48±0.08
Sample C + 0.03% vol.	1.28±0.05	1.36±0.05	1.44±0.03	1.52±0.05	1.68±0.08	1.84±0.05	1.92±0.08
Sample C + 0.05% vol.	1.20±0.03	1.36±0.08	1.44±0.05	1.52±0.08	1.52±0.08	1.68±0.03	1.76±0.05
Sample C + 0.075% vol.	1.20±0.05	1.20±0.02	1.28±0.08	1.28±0.05	1.36±0.03	1.44±0.03	1.44±0.08
Sample C + 0.100% vol.	1.36±0.05	1.36±0.00	1.12±0.05	1.04±0.03	1.20±0.08	1.20±0.05	1.28±0.05
Sample C + 0.120% vol.	1.28±0.08	0.56±0.03	0.64±0.00	0.72±0.03	0.80±0.05	0.88±0.08	1.04±0.03

Table D3 Total Insoluble of hydrocracked gas oil after oxidation at various temperatures (varying in % of nitrogen content)

Spiked sample with Pyridine	Total insoluble after oxidation at various temperatures,mg/100ml.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
Neat Fuel (Sample C)	0.70±0.04	0.72±0.04	0.84±0.06	0.90±0.08	1.27±0.11	1.83±0.18	2.06±0.20
Sample C + 0.03% vol.	0.70±0.03	0.72±0.10	0.87±0.07	0.98±0.09	1.31±0.13	1.87±0.18	2.17±0.22
Sample C + 0.05% vol.	0.70±0.01	0.72±0.09	0.89±0.09	1.13±0.11	1.39±0.14	1.96±0.19	2.22±0.22
Sample C + 0.075% vol.	0.71±0.07	0.73±0.04	0.93±0.09	1.43±0.14	1.51±0.11	2.05±0.21	2.39±0.24
Sample C + 0.100% vol.	0.71±0.09	0.73±0.05	0.97±0.10	1.47±0.15	1.63±0.06	2.17±0.09	2.62±0.26
Sample C + 0.120% vol.	0.73±0.07	0.74±0.06	1.02±0.10	1.62±0.16	1.76±0.02	2.33±0.07	3.01±0.20

Table D4 ASTM Color of hydrocracked gas oil after oxidation at various temperatures (varying in % of nitrogen content)

Spiked sample with Pyridine	ASTM Color after oxidation at various temperatures						
	Non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
Neat Fuel (Sample C)	0	0.25	0.75	0.75	1.50	2.00	2.50
Sample C + 0.03% vol.	0	0.25	0.50	0.75	1.50	2.00	2.25
Sample C + 0.05% vol.	0.25	0.50	0.75	1.00	1.50	2.00	2.25
Sample C + 0.075% vol.	0.25	0.50	0.75	1.25	1.75	2.25	2.50
Sample C + 0.100% vol.	0.25	0.50	1.00	1.50	2.00	2.25	2.75
Sample C + 0.120% vol.	0.25	0.50	1.00	1.25	2.00	2.50	3.00

APPENDIX E

Study of the effects of aromatic content on the stability of diesel fuel

**Table E1 Induction period of diesel fuel after oxidation at various temperatures
(varying in density)**

Sample	Induction period after oxidation at various temperatures ,h					
	25 °C	45°C	65°C	85°C	95°C	100°C
A	21.45±0.21	18.47±0.18	12.36±0.31	10.49±0.10	8.18±0.08	6.42±0.13
B	20.48±0.23	17.26±0.17	10.31±0.10	8.52±0.08	7.41±0.10	5.17±0.12
C	16.00±0.17	12.27±0.12	6.30±0.06	4.30±0.04	3.33±0.20	2.34±0.16
D	18.30±0.18	16.36±0.16	9.49±0.09	7.31±0.07	5.58±0.10	4.37±0.23
E	19.35±0.19	17.00±0.17	10.05±0.12	8.40±0.10	7.20±0.14	5.00±0.11
F	16.57±0.16	13.49±0.13	7.52±0.07	6.49±0.07	4.48±0.05	3.53±0.04
G	16.27±0.15	13.26±0.13	7.37±0.07	5.46±0.05	4.20±0.04	3.30±0.10
H	16.17±0.16	13.26±0.13	8.01±0.08	6.30±0.06	4.10±0.04	3.21±0.03

**Table E2 Peroxide Value (PV) of diesel fuel after after oxidation at various
temperatures (varying in density)**

Sample	Peroxide value(PV) after oxidation at various temperatures, mg/kg.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
A	1.20±0.08	1.12±0.05	0.64±0.03	0.72±0.03	0.80±0.03	0.88±0.03	0.96±0.08
B	1.20±0.05	1.20±0.08	1.28±0.05	1.36±0.08	1.44±0.05	1.52±0.05	1.52±0.03
C	1.44±0.08	1.52±0.08	1.76±0.08	1.92±0.08	2.00±0.08	2.24±0.08	2.48±0.08
D	1.12±0.03	1.20±0.05	1.28±0.08	1.36±0.08	1.44±0.08	1.52±0.08	1.60±0.08
E	1.36±0.05	1.36±0.08	1.44±0.08	1.52±0.05	1.68±0.03	1.76±0.08	1.76±0.08
F	1.44±0.05	1.44±0.05	1.52±0.03	1.60±0.08	1.68±0.08	1.84±0.08	1.92±0.08
G	1.28±0.03	1.36±0.03	1.44±0.05	1.52±0.05	1.68±0.08	1.84±0.05	1.84±0.03
H	1.44±0.03	1.44±0.03	1.52±0.05	1.52±0.05	1.60±0.08	1.76±0.08	1.92±0.05

TableE3 Total Insoluble of diesel fuel after oxidation at various temperatures (varying in density)

Sample	Total insoluble after oxidation at various temperatures,mg/100 ml.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
A	0.30±0.01	0.33±0.02	0.69±0.04	0.96±0.07	2.11±0.18	2.57±0.21	2.68±0.26
B	0.50±0.03	0.51±0.01	0.60±0.03	0.71±0.05	1.11±0.09	1.35±0.13	1.65±0.13
C	0.70±0.04	0.72±0.04	0.84±0.06	0.90±0.08	1.27±0.11	1.83±0.18	2.06±0.20
D	0.50±0.02	0.52±0.03	0.66±0.03	0.73±0.04	1.24±0.14	1.57±0.15	1.65±0.17
E	0.50±0.01	0.54±0.03	0.76±0.02	0.91±0.04	1.93±0.05	2.01±0.20	2.35±0.23
F	0.40±0.04	0.41±0.04	0.57±0.06	0.69±0.07	1.12±0.01	1.49±0.15	1.87±0.19
G	0.50±0.05	0.51±0.05	0.63±0.02	0.77±0.08	1.22±0.05	1.66±0.17	1.92±0.02
H	0.30±0.03	0.33±0.03	0.60±0.05	0.88±0.09	1.76±0.18	1.91±0.19	2.17±0.22

TableE4 ASTM Color of diesel fuel after oxidation at various temperatures (varying in density)

Sample	ASTM Color after oxidation at various temperatures						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
A	0.25	0.75	1.00	1.50	2.00	2.50	2.75
B	0	0.25	0.25	0.75	1.50	2.00	2.00
C	0	0.25	0.25	0.75	1.25	1.75	2.50
D	0.25	0.50	0.5	1.00	1.25	2.00	2.25
E	0.25	0.50	0.75	1.00	1.50	2.25	2.75
F	0.25	0.50	0.75	0.75	1.50	2.00	2.25
G	0.25	0.50	0.75	0.75	1.50	2.00	2.25
H	0.25	0.50	0.75	0.75	1.25	2.25	2.75

APPENDIX F

Study of the effects of component distribution on the stability of diesel fuel

TableF1 Induction period of diesel fuel after oxidation at various temperatures (varying in % component)

Sample	Induction period after oxidation at various temperatures ,h					
	25 °C	45°C	65°C	85°C	95°C	100°C
D	18.30±0.18	16.36±0.16	9.49±0.09	7.31±0.07	5.58±0.10	4.37±0.23
E	19.35±0.16	17.00±0.13	10.05±0.07	8.40±0.07	7.20±0.05	5.00±0.04
F	16.08±0.19	17.07±0.17	7.15±0.12	6.45±0.10	4.48±0.14	3.15±0.11
G	16.27±0.15	13.26±0.13	7.37±0.07	5.46±0.05	4.20±0.04	3.30±0.10
H	16.17±0.16	13.26±0.13	8.01±0.08	6.30±0.06	4.10±0.04	3.21±0.03

Table F2 Peroxide value (PV) of diesel fuel after after oxidation at various temperatures (varying in % component)

Sample	Peroxide value(PV) after oxidation at various temperatures,mg/kg.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
D	1.12±0.03	1.20±0.05	1.28±0.08	1.36±0.08	1.44±0.08	1.52±0.08	1.60±0.08
E	1.36±0.05	1.36±0.05	1.44±0.03	1.52±0.05	1.68±0.08	1.76±0.08	1.76±0.08
F	1.44±0.05	1.44±0.08	1.52±0.08	1.60±0.05	1.68±0.03	1.84±0.08	1.92±0.08
G	1.44±0.03	1.44±0.03	1.52±0.05	1.60±0.05	1.68±0.08	1.84±0.05	1.92±0.03
H	1.44±0.03	1.44±0.03	1.52±0.05	1.52±0.05	1.60±0.08	1.76±0.08	1.92±0.05

Table F3 Total Insoluble of diesel fuel after after oxidation at various temperatures (varying in % component)

Sample	Total insoluble after oxidation at various temperatures,mg/100 ml.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
D	0.50±0.02	0.52±0.03	0.66±0.03	0.73±0.04	1.24±0.14	1.57±0.15	1.65±0.17
E	0.50±0.01	0.54±0.03	0.76±0.02	0.91±0.04	1.93±0.05	2.01±0.20	2.35±0.23
F	0.40±0.04	0.41±0.04	0.57±0.06	0.69±0.07	1.12±0.01	1.49±0.15	1.87±0.19
G	0.50±0.05	0.51±0.05	0.63±0.02	0.77±0.08	1.22±0.01	1.66±0.17	1.92±0.02
H	0.30±0.03	0.33±0.03	0.60±0.05	0.88±0.09	1.76±0.18	1.91±0.19	2.17±0.22

Table F4 ASTM Color of diesel fuel after after oxidation at various temperatures (varying in % component)

Sample	ASTM Color after oxidation at various temperatures						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
D	0.25	0.50	0.50	1.00	1.25	2.00	2.25
E	0.25	0.50	0.75	1.00	1.50	2.25	2.75
F	0.25	0.50	0.75	0.75	1.50	2.00	2.25
G	0.25	0.50	0.75	0.75	1.50	2.00	2.25
H	0.25	0.50	0.75	0.75	1.25	2.25	2.75

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APPENDIX G

Study of the impacts of antioxidant additive on the stability of diesel fuel

1. Varying in the oxidation temperature

Table G1 Induction period of diesel fuel blended with antioxidant additives after oxidation at various temperatures.

Sample + 20 mg/L of each antioxidant additive	Induction period after oxidation at various temperatures ,h					
	25 °C	45°C	65°C	85°C	95°C	100°C
Additive A	19.55±0.19	17.40±0.12	13.49±0.10	11.55±0.11	11.11±0.08	10.30±0.09
Additive B	19.01±0.19	17.20±0.13	11.51±0.08	9.45±0.09	8.47±0.08	8.00±0.07
Additive C	18.30±0.18	16.45±0.16	10.05±0.10	7.36±0.07	6.33±0.06	5.55±0.03
Additive D	18.20±0.17	16.33±0.16	9.50±0.09	7.55±0.07	6.11±0.06	4.40±0.04
Additive E	25.25±0.24	23.47±0.22	19.15±0.19	18.30±0.18	17.41±0.17	15.21±0.15
Additive F	22.18±0.21	20.00±0.17	16.55±0.11	15.27±0.15	13.48±0.13	12.17±0.12
Neat fuel	18.30±0.18	16.36±0.16	9.49±0.09	7.31±0.07	5.58±0.10	4.37±0.23

Table G2 Peroxide value (PV) of diesel fuel blended with antioxidant additives after oxidation at various temperatures.

Sample + 20 mg/L. of each antioxidant additive	Peroxide value(PV) after oxidation at various temperatures, mg/kg.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
Additive A	0.80±0.03	0.88±0.08	0.96±0.05	1.04±0.05	1.12±0.03	1.20±0.05	1.20±0.08
Additive B	1.12±0.03	1.12±0.03	1.20±0.08	1.20±0.03	1.28±0.00	1.36±0.05	1.52±0.08
Additive C	1.04±0.08	1.12±0.05	1.20±0.03	1.28±0.00	1.36±0.05	1.44±0.05	1.60±0.03
Additive D	1.12±0.05	1.20±0.03	1.28±0.08	1.36±0.03	1.44±0.08	1.52±0.05	1.68±0.03
Additive E	0.48±0.05	0.48±0.03	0.56±0.05	0.64±0.00	0.72±0.03	0.80±0.05	0.88±0.05
Additive F	0.56±0.08	0.64±0.03	0.72±0.08	0.72±0.08	0.72±0.05	0.96±0.03	1.04±0.05
Neat fuel	1.12±0.03	1.20±0.05	1.28±0.08	1.36±0.08	1.44±0.08	1.52±0.08	1.60±0.08

**Table G3 Total insoluble of diesel fuel blended with antioxidant additives
after oxidation at various temperatures.**

Sample + 20 mg/L. of each Antioxidant Additive	Total insoluble after oxidation at various temperatures,mg/100 ml.						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
Additive A	0.50±0.01	0.50±0.03	0.55±0.04	0.61±0.06	0.69±0.07	0.77±0.08	0.96±0.09
Additive B	0.50±0.03	0.51±0.01	0.67±0.07	0.79±0.09	1.03±0.12	1.47±0.16	1.61±0.17
Additive C	0.50±0.03	0.51±0.03	0.67±0.05	0.81±0.03	1.20±0.02	1.58±0.02	1.88±0.19
Additive D	0.50±0.02	0.50±0.05	0.58±0.06	0.68±0.07	0.74±0.07	0.81±0.08	1.07±0.11
Additive E	0.50±0.04	0.51±0.05	0.66±0.07	0.78±0.08	0.99±0.07	1.21±0.11	1.29±0.12
Additive F	0.50±0.08	0.50±0.05	0.53±0.03	0.59±0.04	0.61±0.05	0.67±0.06	0.74±0.05
Neat fuel	0.50±0.03	0.52±0.03	0.66±0.05	0.73±0.09	1.24±0.18	1.57±0.19	1.65±0.22

**Table G4 ASTM Color of diesel fuel blended with antioxidant additives
after oxidation at various temperatures.**

Sample + 20 mg/L. of each antioxidant additive	ASTM Color after oxidationat various temperatures						
	non oxidized	25 °C	45°C	65°C	85°C	95°C	100°C
Additive A	0.25	0.25	0.50	0.50	0.75	1.00	1.00
Additive B	0.25	0.50	0.50	1.00	1.25	1.75	2.00
Additive C	0.25	0.50	0.75	1.00	1.50	2.00	2.25
Additive D	0.25	0.25	0.50	0.75	0.75	1.00	1.25
Additive E	0.25	0.25	0.50	0.75	1.00	1.25	1.50
Additive F	0.25	0.25	0.25	0.50	0.50	0.75	0.75
Neat fuel	0.25	0.50	0.50	1.00	1.25	2.00	2.25

2. Varying in the concentrations of antioxidant additive

Table G5 Induction period of diesel fuel after oxidation at 95 ° C
(varying in the concentrations of antioxidant additive)

Type of additives	Induction period of the sample D added with each additive after oxidation at 95 ° C, h						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
Additive A	5.58±0.10	11.11±0.08	11.56±0.11	12.10±0.12	12.58±0.13	13.26±0.13	14.08±0.14
Additive B	5.58±0.10	8.00±0.08	8.46±0.08	9.14±0.09	9.58±0.09	10.20±0.10	11.02±0.11
Additive C	5.58±0.10	6.33±0.06	7.12±0.07	7.48±0.07	7.54±0.07	8.18±0.04	8.46±0.08
Additive D	5.58±0.10	6.11±0.06	6.24±0.06	6.16±0.06	6.20±0.07	6.18±0.03	6.26±0.06
Additive E	5.58±0.10	17.41±0.17	18.20±0.18	18.52±0.19	19.46±0.19	20.04±0.21	21.12±0.17
Additive F	5.58±0.10	13.48±0.13	13.48±0.14	14.18±0.12	14.50±0.14	15.26±0.11	17.02±0.13

Table G6 Peroxide value (PV) of diesel fuel after oxidation at 95 ° C
(varying in the concentrations of antioxidant additive)

Type of additives	Peroxide value(PV) of the sample D added with each additive after oxidation at 95 ° C, mg/kg						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
Additive A	1.52±0.08	1.20±0.05	0.80±0.03	0.64±0.05	0.48±0.05	0.40±0.03	0.24±0.08
Additive B	1.52±0.08	1.36±0.05	1.04±0.05	0.88±0.08	0.64±0.03	0.48±0.05	0.40±0.03
Additive C	1.52±0.08	1.44±0.05	1.12±0.08	0.96±0.08	0.72±0.05	0.56±0.08	0.48±0.05
Additive D	1.52±0.08	1.52±0.05	1.52±0.03	1.52±0.05	1.60±0.03	1.68±0.08	1.52±0.08
Additive E	1.52±0.08	0.80±0.05	0.64±0.03	0.40±0.05	0.24±0.03	0.16±0.05	0.08±0.03
Additive F	1.52±0.08	0.72±0.03	0.72±0.03	0.64±0.03	0.48±0.05	0.32±0.03	0.24±0.00

Table G7 Total insoluble of diesel fuel after oxidation at 95 ° C**(varying in the concentrations of antioxidant additive)**

Type of additives	Total Insoluble of the sample D added with each additive after oxidation at 95 ° C, mg/100 ml						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
Additive A	1.57±0.15	0.77±0.08	0.72±0.06	0.68±0.03	0.61±0.07	0.56±0.03	0.50±0.02
Additive B	1.57±0.15	1.47±0.16	1.50±0.08	1.53±0.15	1.54±0.15	1.61±0.16	1.61±0.15
Additive C	1.57±0.15	1.58±0.02	1.59±0.11	1.61±0.09	1.63±0.16	1.67±0.18	1.70±0.17
Additive D	1.57±0.15	0.81±0.08	0.80±0.06	0.77±0.08	0.65±0.02	0.60±0.05	0.52±0.03
Additive E	1.57±0.15	1.21±0.11	1.30±0.14	1.36±0.12	1.41±0.15	1.50±0.13	1.53±0.15
Additive F	1.57±0.15	0.67±0.06	0.62±0.05	0.62±0.03	0.60±0.02	0.53±0.04	0.44±0.04

Table G8 ASTM Color of diesel fuel after oxidation at 95 ° C**(varying in the concentrations of antioxidant additive)**

Type of additives	ASTM Color of the sample D added with each additive after oxidation at 95 ° C						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
Additive A	2.00	1.00	1.00	0.75	0.75	0.50	0.50
Additive B	2.00	1.75	1.75	1.75	1.75	1.75	2.00
Additive C	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Additive D	2.00	1.00	1.000	0.75	0.75	0.75	0.75
Additive E	2.00	1.25	1.25	1.25	1.25	1.25	1.25
Additive F	2.00	0.75	0.75	0.75	0.50	0.50	0.25

3.Varying in the concentration of N, S-heteroatom containing

Table G9 Physical properties of heavy gas oil added with 20 mg/L of various additives after oxidation at 95 °C.

Test Items	Physical properties of the sample A added with 20 mg/L of various additives after oxidation at 95 °C						
	Additive A	Additive B	Additive C	Additive D	Additive E	Additive F	Neat Fuel
Induction Period at 95 °C, h	13.47±0.14	11.15±0.12	8.20±0.08	8.16±0.09	16.50±0.17	14.11±0.15	8.18±0.08
Peroxide Value(PV),mg/kg	0.64±0.06	0.72±0.05	0.80±0.03	0.88±0.05	0.48±0.08	0.56±0.05	0.88±0.03
ASTM Color	1.00	1.75	2.00	1.00	1.25	0.25	2.50
Total Insoluble,mg/100 ml	0.73±0.04	2.11±0.06	2.41±0.21	1.31±0.14	1.89±0.09	0.62±0.03	2.57±0.21

Table G10 Physical properties of light gas oil added with 20 mg/L of various additives after oxidation at 95 °C.

Test Items	Physical properties of the sample B added with 20 mg/L of various additives after oxidation at 95 °C						
	Additive A	Additive B	Additive C	Additive D	Additive E	Additive F	Neat Fuel
Induction Period at 95 °C , h	10.01±0.12	9.20±0.08	8.30±0.08	8.00±0.06	14.20±0.14	11.30±0.11	7.41±0.10
Peroxide Value(PV),mg/kg	1.28±0.03	1.44±0.05	1.52±0.03	1.52±0.03	0.88±0.08	0.96±0.03	1.52±0.05
ASTM Color	0.75	1.50	1.75	0.75	1.00	0.25	1.75
Total Insoluble,mg/100 ml	0.71±0.03	1.34±0.07	1.36±0.08	1.21±0.12	1.21±0.09	0.67±0.02	1.35±0.13

Table G11 Physical properties of hydrocracked gas oil added with 20 mg/L of various additives after oxidation at 95 °C

Test Items	Physical properties of the sample C added with 20 mg/l of various additives after oxidation at 95 °C						
	Additive A	Additive B	Additive C	Additive D	Additive E	Additive F	Neat Fuel
Induction Period at 95 °C , h	9.50±0.09	7.45±0.08	5.50±0.06	5.00±0.05	12.45±0.11	10.20±0.10	3.33±0.20
Peroxide Value(PV),mg/kg	1.12±0.08	1.20±0.08	1.28±0.03	2.24±0.05	0.96±0.08	1.04±0.08	2.24±0.08
ASTM Color	1.00	1.75	2.00	1.00	1.25	0.25	2.00

Total Insoluble,mg/100 ml	0.96±0.07	1.60±0.08	1.84±0.09	1.53±0.15	1.37±0.07	0.88±0.04	1.83±0.18
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4. Study of component distribution and its density

TableG12 Induction period of diesel fuel blended with antioxidant additives after oxidation at 95 ° C (varying in % component and density)

Test Items	Induction period of each sample added with 20 mg/l of various additives after oxidation at 95 ° C, h						
	Additive A	Additive B	Additive C	Additive D	Additive E	Additive F	Neat Fuel
Sample D	11.11±0.08	8.47±0.08	6.33±0.06	6.11±0.06	17.41±0.17	13.48±0.13	5.58±0.10
Sample E	12.00±0.12	10.50±0.11	6.48±0.06	7.15±0.07	18.13±0.18	14.27±0.14	7.20±0.05
Sample F	11.05±0.11	8.39±0.08	6.30±0.06	6.15±0.06	15.04±0.15	11.58±0.11	4.48±0.14
Sample G	11.10±0.11	8.46±0.04	6.40±0.06	6.02±0.04	16.34±0.15	13.08±0.13	4.20±0.04
Sample H	11.02±0.10	8.40±0.08	6.32±0.03	6.48±0.03	15.50±0.15	11.46±0.12	4.10±0.04

Table G13 Peroxide value (PV) of diesel fuel blended with antioxidant additives after oxidation at 95 ° C (varying in % component and density)

Test Items	Peroxide value(PV) of each sample added with 20 mg/l of various additives after oxidation at 95 ° C, mg/kg						
	Additive A	Additive B	Additive C	Additive D	Additive E	Additive F	Neat Fuel
Sample D	1.20±0.05	1.36±0.05	1.44±0.05	1.52±0.05	0.80±0.05	0.96±0.03	1.52±0.08
Sample E	1.20±0.03	1.44±0.08	1.44±0.08	1.52±0.03	0.96±0.05	1.04±0.03	1.76±0.08
Sample F	1.28±0.05	1.36±0.03	1.52±0.03	1.68±0.05	1.04±0.08	1.12±0.05	1.84±0.08
Sample G	1.20±0.05	1.28±0.03	1.44±0.08	1.52±0.05	1.68±0.08	1.04±0.03	1.84±0.05
Sample H	1.20±0.05	1.28±0.08	1.36±0.05	1.44±0.03	0.96±0.03	1.12±0.05	1.76±0.08

**Table G14 Total insoluble of diesel fuel blended with antioxidant additives
after oxidation at 95 °C (varying in % component and density)**

Test Items	Total insoluble of each sample added with 20 mg/l of various additives after oxidation at 95 °C,mg/100 ml						
	Additive A	Additive B	Additive C	Additive D	Additive E	Additive F	Neat Fuel
Sample D	0.77±0.08	1.47±0.16	1.58±0.02	0.81±0.08	1.21±0.11	0.67±0.06	1.57±0.15
Sample E	0.80±0.04	1.50±0.07	1.98±0.09	0.91±0.09	1.33±0.10	0.71±0.04	2.01±0.20
Sample F	0.78±0.04	1.33±0.11	1.47±0.07	0.88±0.04	1.25±0.12	0.69±0.03	1.49±0.15
Sample G	0.71±0.03	1.29±0.13	1.46±0.07	0.80±0.07	1.20±0.06	0.63±0.06	1.66±0.17
Sample H	0.72±0.03	1.43±0.14	1.77±0.08	0.88±0.04	1.29±0.04	0.69±0.04	1.91±0.19

**Table G 15 ASTM of diesel fuel blended with antioxidant additives
after oxidation at 95 °C (varying in % component and density)**

Test Items	ASTM Color of each sample which is added with 20 mg/L of the various additives after oxidized at 95 °C						
	Additive A	Additive B	Additive C	Additive D	Additive E	Additive F	Neat Fuel
Sample D	0.75	1.75	2.00	1.00	1.25	0.5	2.00
Sample E	1.00	2.00	2.25	1.50	1.75	0.50	2.25
Sample F	0.75	1.75	2.00	1.25	1.50	0.50	2.00
Sample G	0.75	1.75	2.00	1.25	1.50	0.50	2.00
Sample H	1.00	2.00	2.25	1.25	1.75	0.50	2.25

APPENDIX H

5. Varying in reaction time

Table H1 Total insoluble of diesel fuel blended with additive A after oxidation at 25 °C
(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive A after oxidation at 25 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.50	0.49	0.43	0.40	0.36	0.30	0.25	0.30	0.36	0.40	0.43
12 h	0.51	0.50	0.45	0.43	0.40	0.35	0.30	0.35	0.40	0.43	0.45
24 h	0.53	0.51	0.48	0.46	0.43	0.39	0.32	0.39	0.43	0.46	0.48
36 h	0.55	0.53	0.50	0.47	0.44	0.40	0.33	0.40	0.44	0.47	0.50
48 h	0.58	0.55	0.52	0.49	0.47	0.42	0.35	0.42	0.47	0.49	0.52

Table H2 Total insoluble of diesel fuel blended with additive A after oxidation at 45 °C
(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Physical properties of the sample added with the additive A after oxidation at 45 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.60	0.54	0.50	0.46	0.41	0.37	0.32	0.37	0.41	0.46	0.50
12 h	0.65	0.52	0.50	0.48	0.45	0.40	0.34	0.40	0.45	0.48	0.50
24 h	0.70	0.57	0.53	0.50	0.47	0.42	0.37	0.42	0.47	0.50	0.53
36 h	0.73	0.60	0.55	0.51	0.48	0.45	0.38	0.45	0.48	0.51	0.55
48 h	0.76	0.62	0.57	0.54	0.49	0.46	0.41	0.46	0.49	0.54	0.57

Table H3 Total insoluble of diesel fuel blended with additive A after oxidation at 65 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Physical properties of the sample added with the additive A after oxidation at 65 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.80	0.56	0.53	0.50	0.47	0.44	0.43	0.44	0.47	0.50	0.53
12 h	0.84	0.60	0.58	0.53	0.50	0.46	0.45	0.46	0.50	0.53	0.58
24 h	0.87	0.63	0.59	0.55	0.51	0.49	0.47	0.49	0.51	0.55	0.59
36 h	0.90	0.66	0.62	0.58	0.53	0.50	0.48	0.50	0.53	0.58	0.62
48 h	0.93	0.72	0.67	0.61	0.56	0.53	0.51	0.53	0.56	0.61	0.67

Table H4 Total insoluble of diesel fuel blended with additive A after oxidation at 85 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive A after oxidation at 85 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	1.20	0.67	0.65	0.63	0.60	0.58	0.56	0.58	0.60	0.63	0.65
12 h	1.27	0.70	0.68	0.65	0.62	0.60	0.57	0.60	0.62	0.65	0.68
24 h	1.33	0.81	0.76	0.73	0.70	0.66	0.58	0.66	0.70	0.73	0.76
36 h	1.40	0.88	0.77	0.74	0.72	0.67	0.60	0.67	0.72	0.74	0.77
48 h	1.52	0.95	0.80	0.76	0.74	0.70	0.61	0.70	0.74	0.76	0.80

Table H5 Total insoluble of diesel fuel blended with additive A after oxidation at 95 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive A after oxidation at 95 °C									
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L			
6 h	1.68	0.70	0.69	0.65	0.63	0.61	0.57			
12 h	1.71	0.73	0.70	0.67	0.66	0.63	0.59			
24 h	1.76	0.84	0.74	0.71	0.68	0.65	0.60			
36 h	1.82	0.91	0.80	0.74	0.69	0.66	0.61			
48 h	1.89	0.97	0.82	0.88	0.81	0.76	0.63			

Table H6 Total insoluble of diesel fuel blended with additive A after oxidation at 100 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive A after oxidation at 100 °C									
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L			
6 h	2.03	0.85	0.74	0.72	0.69	0.66	0.61			
12 h	2.06	0.89	0.79	0.75	0.70	0.67	0.61			
24 h	2.11	0.93	0.80	0.76	0.73	0.69	0.62			
36 h	2.18	0.97	0.90	0.80	0.76	0.73	0.63			
48 h	2.24	1.16	0.92	0.83	0.80	0.77	0.66			

Table H7 Total insoluble of diesel fuel blended with additive B after oxidation at 25 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Physical Properties of the sample added with the additive B after oxidation at 25 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.50	0.48	0.47	0.45	0.43	0.41	0.40	0.41	0.43	0.45	0.47
12 h	0.51	0.49	0.47	0.46	0.44	0.43	0.41	0.43	0.44	0.46	0.47
24 h	0.53	0.52	0.50	0.48	0.46	0.45	0.43	0.45	0.46	0.48	0.50
36 h	0.55	0.54	0.53	0.50	0.49	0.47	0.46	0.47	0.49	0.50	0.53
48 h	0.58	0.57	0.56	0.53	0.51	0.50	0.49	0.50	0.51	0.53	0.56

Table H8 Total insoluble of diesel fuel blended with additive B after oxidation at 45 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive B after oxidation at 45 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.60	0.59	0.57	0.55	0.53	0.51	0.49	0.51	0.53	0.55	0.57
12 h	0.65	0.64	0.62	0.59	0.56	0.53	0.51	0.53	0.56	0.59	0.62
24 h	0.70	0.65	0.63	0.61	0.58	0.55	0.54	0.55	0.58	0.61	0.63
36 h	0.73	0.67	0.64	0.63	0.61	0.6	0.58	0.6	0.61	0.63	0.64
48 h	0.76	0.69	0.66	0.64	0.63	0.63	0.61	0.63	0.63	0.64	0.66

Table H9 Total insoluble of diesel fuel blended with additive B after oxidation at 65 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive B after oxidation at 65 °C												
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L	20 mg/L	0 mg/L
6 h	0.80	0.77	0.75	0.72	0.68	0.64	0.60	0.64	0.68	0.72	0.75	0.77	0.80
12 h	0.84	0.82	0.79	0.75	0.71	0.67	0.63	0.67	0.71	0.75	0.79	0.82	0.84
24 h	0.87	0.84	0.81	0.78	0.75	0.71	0.67	0.71	0.75	0.78	0.81	0.84	0.87
36 h	0.90	0.86	0.83	0.80	0.77	0.74	0.72	0.74	0.77	0.80	0.83	0.86	0.90
48 h	0.93	0.90	0.87	0.84	0.80	0.78	0.76	0.78	0.80	0.84	0.87	0.90	0.93

Table H10 Total insoluble of diesel fuel blended with additive B after oxidation at 85 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive B after oxidation at 85 °C												
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L	20 mg/L	0 mg/L
6 h	1.20	1.07	1.02	0.96	0.90	0.83	0.74	0.83	0.90	0.96	1.02	1.07	1.20
12 h	1.27	1.10	1.04	0.99	0.92	0.84	0.77	0.84	0.92	0.99	1.04	1.10	1.27
24 h	1.33	1.18	1.10	1.02	0.94	0.87	0.82	0.87	0.94	1.02	1.10	1.18	1.33
36 h	1.40	1.22	1.16	1.09	1.00	0.92	0.87	0.92	1.00	1.09	1.16	1.22	1.40
48 h	1.52	1.36	1.27	1.19	1.10	1.03	0.96	1.03	1.10	1.19	1.27	1.36	1.52

Table H11 Total insoluble of diesel fuel blended with additive B after oxidation at 95 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive B after oxidation at 95 °C						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
6 h	1.68	1.45	1.38	1.30	1.22	1.14	1.05
12 h	1.71	1.56	1.48	1.39	1.30	1.18	1.09
24 h	1.76	1.63	1.54	1.46	1.35	1.22	1.14
36 h	1.82	1.67	1.58	1.49	1.40	1.31	1.23
48 h	1.89	1.72	1.63	1.54	1.46	1.37	1.30

Table H12 Total insoluble of diesel fuel blended with additive B after oxidation at 100 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive B after oxidation at 100 °C						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
6 h	2.03	1.64	1.53	1.45	1.36	1.28	1.21
12 h	2.06	1.70	1.60	1.51	1.42	1.34	1.27
24 h	2.11	1.76	1.68	1.60	1.48	1.40	1.32
36 h	2.18	1.88	1.80	1.70	1.58	1.15	1.39
48 h	2.24	1.97	1.89	1.80	1.68	1.56	1.44

Table H13 Total insoluble of diesel fuel blended with additive C after oxidation at 25 ° C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive C after oxidation at 25 ° C						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
6 h	0.50	0.48	0.47	0.46	0.45	0.43	0.42
12 h	0.51	0.50	0.49	0.48	0.46	0.44	0.43
24 h	0.53	0.52	0.50	0.49	0.47	0.46	0.45
36 h	0.55	0.53	0.51	0.50	0.48	0.47	0.47
48 h	0.58	0.58	0.56	0.55	0.54	0.52	0.50

Table H14 Total insoluble of diesel fuel blended with additive C after oxidation at 45 ° C

(varying in the reaction time)

Sample D after oxidized at each reaction time, h	Total insoluble of the sample added with the additive C after oxidation at 45 ° C						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
6 h	0.60	0.58	0.57	0.56	0.54	0.52	0.50
12 h	0.65	0.63	0.6	0.58	0.56	0.52	0.53
24 h	0.70	0.68	0.65	0.63	0.60	0.54	0.55
36 h	0.73	0.70	0.68	0.66	0.63	0.58	0.58
48 h	0.76	0.74	0.71	0.69	0.67	0.64	0.62

Table H15 Total insoluble of diesel fuel blended with additive C after oxidation at 65 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive C after oxidation at 65 °C									
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L
6 h	0.80	0.77	0.75	0.72	0.70	0.67	0.64	0.67	0.70	0.72
12 h	0.84	0.80	0.77	0.74	0.72	0.70	0.67	0.70	0.72	0.74
24 h	0.87	0.83	0.80	0.78	0.75	0.73	0.72	0.73	0.75	0.78
36 h	0.90	0.87	0.84	0.81	0.78	0.77	0.74	0.77	0.78	0.81
48 h	0.93	0.90	0.88	0.85	0.82	0.80	0.77	0.80	0.82	0.85

Table H16 Total insoluble of diesel fuel blended with additive C after oxidation at 85 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive C after oxidation at 85 °C									
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L
6 h	1.20	1.17	1.12	1.05	0.98	0.89	0.80	0.89	0.98	1.05
12 h	1.27	1.24	1.18	1.10	1.00	0.90	0.81	0.90	1.00	1.10
24 h	1.33	1.27	1.20	1.12	1.03	0.94	0.85	0.94	1.03	1.12
36 h	1.40	1.33	1.25	1.17	1.09	1.00	0.89	1.00	1.09	1.17
48 h	1.52	1.44	1.35	1.28	1.20	1.11	1.01	1.11	1.20	1.28

Table H17 Total insoluble of diesel fuel blended with additive C after oxidation at 95 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive C after oxidation at 95 °C						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
6 h	1.68	1.54	1.48	1.40	1.33	1.24	1.13
12 h	1.71	1.62	1.54	1.46	1.37	1.29	1.19
24 h	1.76	1.65	1.57	1.50	1.41	1.33	1.25
36 h	1.82	1.71	1.63	1.55	1.47	1.38	1.29
48 h	1.89	1.75	1.68	1.60	1.51	1.43	1.33

Table H18 Total insoluble of diesel fuel blended with additive C after oxidation at 100 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive C after oxidation at 100 °C						
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L
6 h	2.03	1.90	1.80	1.67	1.54	1.42	1.31
12 h	2.06	1.92	1.83	1.75	1.65	1.57	1.45
24 h	2.11	1.96	1.87	1.79	1.70	1.61	1.50
36 h	2.18	1.98	1.90	1.81	1.74	1.65	1.57
48 h	2.24	2.00	1.92	1.83	1.78	1.69	1.60

Table H19 Total insoluble of diesel fuel blended with additive D after oxidation at 25 ° C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive D after oxidation at 25 ° C							
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	
6 h	0.50	0.48	0.44	0.41	0.37	0.31	0.27	
12 h	0.51	0.50	0.46	0.44	0.42	0.36	0.30	
24 h	0.53	0.51	0.49	0.46	0.42	0.38	0.32	
36 h	0.55	0.54	0.51	0.48	0.43	0.40	0.33	
48 h	0.58	0.56	0.53	0.50	0.48	0.43	0.34	

Table H20 Total insoluble of diesel fuel blended with additive D after oxidation at 45 ° C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive D after oxidation at 45 ° C							
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	
6 h	0.60	0.55	0.51	0.48	0.43	0.38	0.31	
12 h	0.65	0.56	0.53	0.50	0.48	0.42	0.34	
24 h	0.70	0.58	0.55	0.51	0.50	0.46	0.35	
36 h	0.73	0.61	0.57	0.54	0.52	0.46	0.37	
48 h	0.76	0.63	0.58	0.56	0.53	0.48	0.38	

Table H21 Total insoluble of diesel fuel blended with additive D after oxidation at 65 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive D after oxidation at 65 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.80	0.68	0.63	0.57	0.50	0.44	0.38	0.44	0.50	0.57	0.63
12 h	0.84	0.72	0.65	0.62	0.56	0.48	0.40	0.48	0.56	0.62	0.65
24 h	0.87	0.73	0.68	0.66	0.63	0.53	0.44	0.53	0.63	0.66	0.68
36 h	0.90	0.76	0.70	0.67	0.65	0.56	0.48	0.56	0.65	0.67	0.70
48 h	0.93	0.78	0.73	0.70	0.68	0.58	0.49	0.58	0.68	0.70	0.73

Table H22 Total insoluble of diesel fuel blended with additive D after oxidation at 85 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive D after oxidation at 85 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	1.20	0.70	0.67	0.60	0.54	0.48	0.42	0.48	0.54	0.60	0.67
12 h	1.27	0.72	0.69	0.65	0.60	0.52	0.45	0.52	0.60	0.65	0.69
24 h	1.33	0.76	0.72	0.67	0.60	0.55	0.48	0.55	0.60	0.67	0.72
36 h	1.40	0.79	0.75	0.70	0.64	0.58	0.49	0.58	0.64	0.70	0.75
48 h	1.52	0.82	0.79	0.72	0.65	0.60	0.54	0.60	0.65	0.72	0.79

Table H23 Total insoluble of diesel fuel blended with additive D after oxidation at 95 ° C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive D after oxidation at 95 ° C							
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	120 mg/L
6 h	1.68	0.80	0.78	0.75	0.63	0.59	0.50	0.50
12 h	1.71	0.96	0.87	0.82	0.71	0.64	0.52	0.52
24 h	1.76	1.03	1.00	0.94	0.80	0.68	0.53	0.53
36 h	1.82	1.12	1.06	0.98	0.90	0.71	0.59	0.59
48 h	1.89	1.21	1.12	1.06	0.97	0.83	0.67	0.67

Table H24 Total insoluble of diesel fuel blended with additive D after oxidation at 100 ° C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive D after oxidation at 100 ° C							
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	120 mg/L
6 h	2.03	1.14	1.10	1.00	0.89	0.72	0.60	0.60
12 h	2.06	1.18	1.12	1.05	0.94	0.73	0.62	0.62
24 h	2.11	1.23	1.17	1.10	1.01	0.86	0.70	0.70
36 h	2.18	1.27	1.20	1.13	1.03	0.88	0.76	0.76
48 h	2.24	1.33	1.22	1.17	1.09	0.92	0.81	0.81

Table H25 Total insoluble of diesel fuel blended with additive E after oxidation at 25 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive E after oxidation at 25 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.50	0.49	0.47	0.43	0.41	0.40	0.39	0.40	0.41	0.43	0.47
12 h	0.51	0.50	0.49	0.47	0.45	0.43	0.41	0.43	0.45	0.47	0.49
24 h	0.53	0.51	0.50	0.48	0.46	0.45	0.44	0.45	0.46	0.48	0.50
36 h	0.55	0.53	0.51	0.49	0.48	0.46	0.46	0.46	0.48	0.49	0.51
48 h	0.58	0.57	0.55	0.53	0.51	0.50	0.48	0.50	0.51	0.53	0.55

Table H26 Total insoluble of diesel fuel blended with additive E after oxidation at 45 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive E after oxidation at 45 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.60	0.58	0.56	0.53	0.51	0.49	0.47	0.49	0.51	0.53	0.56
12 h	0.65	0.63	0.61	0.59	0.57	0.54	0.50	0.54	0.57	0.59	0.61
24 h	0.70	0.67	0.64	0.61	0.58	0.56	0.53	0.56	0.58	0.61	0.64
36 h	0.73	0.70	0.68	0.65	0.62	0.58	0.54	0.58	0.62	0.65	0.68
48 h	0.76	0.73	0.70	0.65	0.65	0.61	0.57	0.61	0.65	0.65	0.70

Table H27 Total insoluble of diesel fuel blended with additive E after oxidation at 65 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive E after oxidation at 65 °C									
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L
6 h	0.80	0.77	0.74	0.70	0.66	0.62	0.58	0.62	0.66	0.70
12 h	0.84	0.80	0.77	0.73	0.69	0.64	0.69	0.64	0.69	0.73
24 h	0.87	0.82	0.80	0.77	0.73	0.70	0.65	0.70	0.73	0.77
36 h	0.90	0.84	0.81	0.79	0.76	0.72	0.68	0.72	0.76	0.79
48 h	0.93	0.78	0.73	0.70	0.68	0.58	0.49	0.58	0.68	0.70

Table H28 Total insoluble of diesel fuel blended with additive E after oxidation at 85 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive E after oxidation at 85 °C									
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L
6 h	1.20	0.91	0.90	0.83	0.78	0.73	0.70	0.73	0.78	0.83
12 h	1.27	0.95	0.88	0.84	0.79	0.74	0.72	0.74	0.79	0.84
24 h	1.33	1.08	1.02	0.96	0.90	0.83	0.75	0.83	0.90	0.96
36 h	1.40	1.21	1.14	1.08	1.01	0.93	0.85	0.93	1.01	1.08
48 h	1.52	1.36	1.25	1.17	1.08	1.00	0.89	1.00	1.08	1.17

Table H29 Total insoluble of diesel fuel blended with additive E after oxidation at 95 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive E after oxidation at 95 °C									
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L			
6 h	1.68	1.18	1.13	1.06	1.00	0.94	0.87			
12 h	1.71	1.20	1.14	1.09	1.02	0.96	0.90			
24 h	1.76	1.30	1.22	1.15	1.07	0.99	0.91			
36 h	1.82	1.36	1.28	1.20	1.12	1.01	0.94			
48 h	1.89	1.43	1.36	1.29	1.21	1.13	1.05			

Table H30 Total insoluble of diesel fuel blended with additive E after oxidation at 100 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive E after oxidation at 100 °C									
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L			
6 h	2.03	1.21	1.13	1.07	1.01	0.96	0.92			
12 h	2.06	1.24	1.16	1.09	1.03	0.98	1.04			
24 h	2.11	1.35	1.29	1.22	1.15	1.09	1.06			
36 h	2.18	1.39	1.31	1.26	1.20	1.13	1.09			
48 h	2.24	1.49	1.40	1.32	1.27	1.21	1.14			

Table H31 Total insoluble of diesel fuel blended with additive F after oxidation at 25 °C
(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the added with the additive F after oxidation at 25 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.50	0.48	0.43	0.38	0.30	0.22	0.14	0.22	0.30	0.38	0.43
12 h	0.51	0.50	0.46	0.40	0.32	0.23	0.18	0.23	0.32	0.40	0.46
24 h	0.53	0.51	0.46	0.41	0.34	0.27	0.20	0.27	0.34	0.41	0.46
36 h	0.55	0.53	0.47	0.42	0.36	0.29	0.21	0.29	0.36	0.42	0.47
48 h	0.58	0.54	0.48	0.42	0.37	0.31	0.24	0.31	0.37	0.42	0.48

Table H32 Total insoluble of diesel fuel blended with additive F after oxidation at 45 °C
(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive F after oxidation at 45 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.60	0.53	0.48	0.43	0.37	0.30	0.22	0.30	0.37	0.43	0.48
12 h	0.65	0.54	0.50	0.44	0.38	0.32	0.24	0.32	0.38	0.44	0.50
24 h	0.70	0.55	0.54	0.53	0.46	0.36	0.27	0.36	0.46	0.53	0.54
36 h	0.73	0.57	0.55	0.54	0.48	0.37	0.30	0.37	0.48	0.54	0.55
48 h	0.76	0.58	0.57	0.56	0.51	0.42	0.32	0.42	0.51	0.56	0.57

Table H33 Total insoluble of diesel fuel blended with additive F after oxidation at 65 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive F after oxidation at 65 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	0.80	0.55	0.54	0.52	0.49	0.39	0.31	0.39	0.49	0.52	0.54
12 h	0.84	0.57	0.55	0.53	0.52	0.44	0.34	0.44	0.52	0.53	0.55
24 h	0.87	0.59	0.56	0.55	0.54	0.45	0.37	0.45	0.54	0.55	0.56
36 h	0.90	0.60	0.58	0.56	0.54	0.50	0.40	0.50	0.54	0.56	0.58
48 h	0.93	0.62	0.60	0.57	0.56	0.54	0.42	0.54	0.56	0.57	0.60

Table H34 Total insoluble of diesel fuel blended with additive F after oxidation at 85 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive F after oxidation at 85 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	1.20	0.59	0.56	0.54	0.50	0.49	0.46	0.49	0.50	0.54	0.56
12 h	1.27	0.60	0.58	0.55	0.53	0.50	0.48	0.50	0.53	0.55	0.58
24 h	1.33	0.63	0.61	0.58	0.56	0.53	0.51	0.53	0.56	0.58	0.61
36 h	1.40	0.66	0.63	0.60	0.57	0.55	0.54	0.55	0.57	0.60	0.63
48 h	1.52	0.71	0.67	0.64	0.60	0.58	0.57	0.58	0.60	0.64	0.67

Table H35 Total insoluble of diesel fuel blended with additive F after oxidation at 95 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive F after oxidation at 95 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	1.68	0.62	0.57	0.53	0.50	0.49	0.49	0.49	0.50	0.53	0.57
12 h	1.71	0.66	0.61	0.60	0.57	0.51	0.50	0.51	0.57	0.60	0.61
24 h	1.76	0.69	0.64	0.62	0.59	0.56	0.54	0.56	0.59	0.62	0.64
36 h	1.82	0.71	0.67	0.64	0.60	0.57	0.58	0.57	0.60	0.64	0.67
48 h	1.89	0.74	0.70	0.67	0.64	0.61	0.60	0.61	0.64	0.67	0.70

Table H36 Total insoluble of diesel fuel blended with additive F after oxidation at 100 °C

(varying in the reaction time)

Sample D after oxidation at each reaction time, h	Total insoluble of the sample added with the additive F after oxidation at 100 °C										
	0 mg/L	20 mg/L	40 mg/L	60 mg/L	80 mg/L	100 mg/L	120 mg/L	100 mg/L	80 mg/L	60 mg/L	40 mg/L
6 h	2.03	0.70	0.68	0.63	0.60	0.58	0.57	0.58	0.60	0.63	0.68
12 h	2.06	0.74	0.70	0.67	0.63	0.60	0.59	0.60	0.63	0.67	0.70
24 h	2.11	0.81	0.76	0.70	0.64	0.61	0.61	0.61	0.64	0.70	0.76
36 h	2.18	0.86	0.80	0.77	0.72	0.66	0.62	0.66	0.72	0.77	0.80
48 h	2.24	0.94	0.88	0.80	0.74	0.67	0.63	0.67	0.74	0.80	0.88

Table H37 Total insoluble of diesel fuel blended with unknown additives after oxidation at

various temperatures (varying in the reaction time)

Sample I after oxidation at each reaction time, h	Total insoluble after oxidation at various temperature, mg/100 ml							
	25°C	45°C	65°C	85°C	95°C	100°C		
6 h	0.51	0.57	0.63	0.68	0.74	0.81		
12 h	0.53	0.59	0.67	0.71	0.79	0.87		
24 h	0.54	0.60	0.69	0.74	0.83	0.92		
36 h	0.56	0.63	0.71	0.78	0.88	0.98		
48 h	0.59	0.66	0.73	0.81	0.92	1.03		

APPENDIX I

The impacts of the combination additive on the stability of diesel fuel

Table I1 The impact of combination additive on the stability of diesel fuel after oxidation at 95 °

Test Items	Physical properties of the sample D added with 100 mg/L of the combination additives after oxidation at 95 ° C										
	Antioxidant additive					Combination additive					Natural antioxidant (Sample A)
	Additive A	Additive B	Additive C	Additive D	Additive E	Additive F					
Induction period at 95 ° C ,h	13.26±0.13	10.20±0.10	8.18±0.04	6.18±0.03	20.04±0.21	15.26±0.16	18.56±0.16			8.18±0.08	
Peroxide value(PV),mg/kg	0.40±0.03	0.48±0.05	0.56±0.08	1.68±0.08	0.16±0.05	0.32±0.24	0.24±0.11			0.88±0.03	
ASTM Color	0.50	1.75	2.00	0.75	1.25	0.50	0.50			2.50	
Total insoluble,mg/100 mL	0.56±0.03	1.61±0.16	1.67±0.18	0.60±0.05	1.50±0.13	0.53±0.05	0.51±0.05			2.57±0.21	

APPENDIX J

Table J 1 % Hydrocracking gas oil (HGGO) fraction in diesel fuels.

Sample	% Distillate fraction			Sample	% Distillate fraction		
	Heavy Gas Oil (HGO)	Light Gas Oil (LGO)	Hydrocracked Gas Oil (HGGO)		Heavy Gas Oil (HGO)	Light Gas Oil (LGO)	Hydrocracked Gas Oil (HGGO)
A	100	0	0	J	50	25	25
B	0	100	0	K	20	10	70
C	0	0	100	L	30	30	40
D	65	10	25	M	0	10	90
E	70	10	20	N	50	0	50
F	65	5	30	O	10	10	80
G	65	15	20	P	40	10	50
H	60	10	30	Q	20	20	60
I	65	10	25				

Table J 2 ASTM Color of diesel fuel at each storage condition.

Sample	before	After settled in at each storage conditions			Sample	Before	After settled in at each storage conditions		
		Dark	Room Temp.	Outdoor			Dark	Room Temp.	Outdoor
A	0.25	0.75	1.50	2.25	E	0.25	0.75	1.00	2.50
A+100 mg/L of Additive A	0.25	0.50	0.75	1.00	F	0.25	0.75	1.00	2.75
A+100 mg/L of Additive B	0.25	0.50	1.00	1.50	G	0.25	0.75	1.00	2.25
A+100 mg/L of Additive D	0.25	0.75	1.25	1.75	H	0.25	0.75	1.00	2.5
A+100 mg/L of Additive (A+D)	0.25	0.25	0.75	1.25	I	0.50	0.75	1.00	2.5
A+100 mg/L of Additive(B+ D)	0.25	0.50	1.00	1.50	J	0	0.50	0.50	2.25
B	0	0.50	0.50	0.75	K	0	0.50	0.75	5.0
C	0	0.50	1.00	5.75	L	0.25	0.50	0.75	4.25
C+100 mg/L of Additive A	0.25	0.25	0.50	2.00	M	0	0.50	1.00	5.50
C+100 mg/L of Additive B	0.25	0.25	0.75	2.25	N	0.25	0.75	1.25	4.00
C+100 mg/L of Additive D	0.25	0.50	0.75	2.75	O	0	0.50	1.00	5.25
C+100 mg/L of Additive (A+D)	0.25	0.25	0.50	1.75	P	0.25	0.50	1.00	3.75
C+100 mg/L of Additive(B+ D)	0.25	0.25	0.50	2.00	Q	0.25	0.50	1.00	4.50
D	0.25	0.75	1.25	2.25					
D+100 mg/L of Additive A	0.25	0.50	0.50	1.00					
D+100 mg/L of Additive B	0.25	0.50	0.75	1.25					
D+100 mg/L of Additive D	0.25	0.75	1.00	1.50					
D+100 mg/L of Additive (A+D)	0.25	0.50	0.50	0.75					
D+100 mg/L of Additive(B+ D)	0.25	0.50	0.75	1.25					

Table J 3 Total insoluble of diesel fuel at each storage condition.

Sample	Before		After settled in at each storage conditions			Sample	Before		After settled in at each storage conditions		
			Dark	Room Temp.	Outdoor				Dark	Room Temp.	Outdoor
A	0.30±0.01		0.33±0.02	0.50±0.01	2.89±0.20	E	0.50±0.02	1.63±0.16	2.37±0.24		
A+100 mg/L of Additive A	-		0.36±0.02	0.37±0.05	0.98±0.05	F	0.40±0.01	1.72±0.09	2.53±0.13		
A+100 mg/L of Additive B	-		0.40±0.04	0.43±0.03	2.00±0.10	G	0.50±0.03	1.56±0.08	2.28±0.12		
A+100 mg/L of Additive D	-		0.35±0.03	0.38±0.02	1.35±0.13	H	0.30±0.01	1.62±0.16	2.41±0.20		
A+100 mg/L of Additive (A+D)	-		0.31±0.02	0.34±0.03	0.77±0.04	I	0.50±0.03	1.59±0.16	2.33±0.19		
A+100 mg/L of Additive(B+ D)	-		0.34±0.01	0.39±0.02	1.24±0.06	J	0.47±0.03	1.53±0.14	2.14±0.20		
B	0.50±0.03		0.51±0.02	0.52±0.03	1.20±0.07	K	0.71±0.04	1.94±0.11	4.82±0.41		
C	0.72±0.02		1.80±0.13	2.16±0.12	13.00±0.61	L	0.57±0.03	1.64±0.13	2.31±0.23		
C+100 mg/L of Additive A	-		0.82±0.04	0.91±0.05	4.37±0.27	M	0.74±0.03	2.69±0.21	7.70±0.59		
C+100 mg/L of Additive B	-		1.68±0.12	2.07±0.14	6.43±0.33	N	0.61±0.03	1.81±0.18	4.64±0.26		
C+100 mg/L of Additive D	-		1.47±0.11	1.83±0.17	3.16±0.18	O	0.70±0.04	2.38±0.21	6.51±0.43		
C+100 mg/L of Additive (A+D)	-		0.77±0.04	0.80±0.03	2.87±0.28	P	0.58±0.03	1.95±0.17	3.43±0.31		
C+100 mg/L of Additive(B+ D)	-		1.51±0.08	1.72±0.16	3.81±0.35	Q	0.63±0.03	1.71±0.08	3.99±0.30		
D	0.50±0.05		0.74±0.04	1.58±0.16	2.11±0.21						
D+100 mg/L of Additive A	-		0.63±0.03	0.81±0.03	1.47±0.14						
D+100 mg/L of Additive B	-		0.66±0.03	1.18±0.05	1.93±0.15						
D+100 mg/L of Additive D	-		0.64±0.03	1.06±0.10	1.48±0.15						
D+100 mg/L of Additive (A+D)	-		0.63±0.02	0.75±0.07	1.37±0.14						
D+100 mg/L of Additive(B+ D)	-		0.67±0.01	1.01±0.09	1.40±0.07						

VITA

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