# CHAPTER 4

## RESULTS AND DISCUSSION

In this study, desulfurization experiment of high speed diesel is presented in three parts. In part one, oxidation reaction of sulfur compound in high speed diesel is studied using two oxidants, hydroperoxide and peroxy acid, to find suitable conditions for oxidation reaction and to compare the oxidation reaction by both oxidants.

Hydrogen peroxide and tert-butyl hydroperoxide are chosen to represent oxidation agents in hydroperoxide group and peracetic acid is chosen to represent oxidation agents in peroxy acid group. Peracetic acid is chosen to represent oxidation agents in peroxy acid group. From the study of Amir and William (1978), hydrogen peroxide and tert-butyl hydroperoxide are selected as hydroperoxide reagents. Hydrogen peroxide is suitable for aromatic sulfur compound and tert-butyl hydroperoxide is for cyclo sulfur compound. Peracetic acid is suitable for aromatic sulfur compound and cyclo sulfur compound. Solvent for oxidation reaction of sulfur compound are acetic acid ethanol and methanol. Oxidation reaction by using hydrogen peroxide as oxidant has been used with solvent at 90 °C and by tert-butyl hydroperoxide as oxidant has been used with solvent at 60 °C. This oxidation reaction is in batch reactor by using stirring speed 1600 cycle per minute and temperature-controlled bath.

Not only that but also it is for studying second, third oxidation reaction and effecting of that process to physical properties of high speed diesel after oxidation reaction are investigated. Studied properties are sulfur content, viscosity, flash point, pour point, colour, aromatic content and distillation.

Part two presents emphasise of removal sulfur compound which has already reacted through oxidation reaction using solvent extraction method. Deviations from Raoult's law in solution behavior have been attributed to many characteristics such as

molecular size and shape, but the strongest deviation appears to be due to hydrogen bonding and electron donor-acceptor interactions. Robbins (1980) presented a table of these interaction, Table 2.2, that probides a qualitative guide to solvent selection for liquid-liquid extraction. Solvents used in this thesis are methanol, acetic acid, ammonia and ethanolamine. Each solvent is mixed with high speed diesel at various ratio and its efficiency is compared with others.

Part three is comparative study of physical properties of high speed diesel such as density, viscosity, flash point, colour, sulfur content, aromatic content and distillation range. High speed diesels before passing through desulfurization unit are taken from Rayong Refinery and Thaioil Refinery. The physical properties of high speed diesel from Rayong Refinery and Thaioil Refinery are shown in Table 4.1

## 4.1 INSTRUMENT AND EXPERIMENTAL ERROR.

X-Ray instrument is used to determine sulfur content of high speed diesel following ASTM D4254. Accuracy of the instrument is found by analysis of same samples for five times. It is found that the accuracy is within 2 percent, as shown in Table 4.2.

Accuracy experimental method is also found by conducting the experiment at same conditions for four times. It is found that the accuracy is within 3 percent, as shown in Table 4.2.

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Table 4.1 The physical properties of high speed diesel from Rayong Refinery and Thaioil Refinery.

| Physical property | Test method | High speed diesel (Thaioil Refinary) | High speed diesel (Rayong Refinary) |
|---|---|---|---|
| Density @15 °C (kg/l.) | ASTM D-1298 | 0.8552 | 0.8542 |
| Viscosity @40 °C (cst.) | ASTM D-445 | 4.27 | 5.51 |
| Flash Point,PMCC (°C. ) | ASTM D-93 | 102 | 98 |
| Pour point (°C. ) | ASTM D-97 | 0.0 | 3.0 |
| Colour (ASTM Colour) | ASTM D-1500 | L 1.0 | 0.5 |
| Sulfur Content (%wt.) | ASTM D-4294 | 0.63 | 0.92 |
| Aromatic content (%wt.) | ASTM D-1319 | 12.50 | 23.08 |
| Distillation (°C. ) | ASTM D-86 | | |
| IBP | | 219.8 | 241.3 |
| 10% | | 252.7 | 277.0 |
| 50% | | 297.9 | 323.9 |
| 90% | | 361.4 | 358.0 |
| End Point | | 386.9 | 365.4 |

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Table 4.2 Precision and variation of sulfur content in high speed diesel.

| | Sulfur content (%wt.) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1nd. Oxidation reaction by hydrogen peroxide. | | | | | | | | | | |
| | Before 1st. oxidation reaction process. | | | | | | After 1st. oxidation reaction process. | | | | |
| | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | average. | Batch 1 | Batch 2 | Batch 3 | Batch 4 | average. |
| High speed diesel (Thaioil Refinary) | 0.62 | 0.64 | 0.63 | 0.61 | 0.64 | 0.63±0.02 | 0.28 | 0.3 | 0.35 | 0.34 | 0.32±0.04 |
| High speed diesel (Rayong Refinary) | 0.91 | 0.91 | 0.92 | 0.92 | 0.94 | 0.92±0.02 | 0.43 | 0.46 | 0.44 | 0.39 | 0.43±0.04 |
| | 2nd. Oxidation reaction by hydrogen peroxide. | | | | | | | | | | |
| | Before 2st. oxidation reaction process. | | | | | | After 2st. oxidation reaction process. | | | | |
| | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | average. | Batch 1 | Batch 2 | Batch 3 | Batch 4 | average. |
| High speed diesel (Thaioil Refinary) | 0.32 | 0.32 | 0.33 | 0.32 | 0.32 | 0.32±0.01 | 0.18 | 0.15 | 0.15 | 0.16 | 0.16±0.02 |
| High speed diesel (Rayong Refinary) | 0.43 | 0.42 | 0.42 | 0.46 | 0.43 | 0.43±0.02 | 0.2 | 0.21 | 0.22 | 0.24 | 0.22±0.02 |
| | Oxidation reaction by peracetic acid | | | | | | | | | | |
| | Before oxidation reaction process. | | | | | | After oxidation reaction process. | | | | |
| | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | average. | Batch 1 | Batch 2 | Batch 3 | Batch 4 | average. |
| High speed diesel (Thaioil Refinary) | 0.61 | 0.63 | 0.62 | 0.60 | 0.63 | 0.62±0.02 | 0.50 | 0.51 | 0.48 | 0.49 | 0.49±0.02 |
| High speed diesel (Rayong Refinary) | 0.91 | 0.91 | 0.92 | 0.92 | 0.94 | 0.92±0.02 | 0.74 | 0.70 | 0.70 | 0.69 | 0.71±0.03 |

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## 4.2 CONDITION OF OXIDATION REACTION USING PEROXIDE AS OXIDANT.

This investigation consists of suitable condition for oxidation reaction of sulfur compound in high speed diesel by using two oxidants. Hydrogen peroxide and tert-butyl hydro-peroxide are selected as hydroperoxide reagents. Solvents for this study are acetic acid and ethanol. Table 4.3 shows results of the experiments which consists of sulfur content in high speed diesel and its colour. High speed diesel from Thaioil Refinery having sulfur content of 0.63% is used to find condition of oxidation reaction using hydrogen peroxide and tert-butyl hydro-peroxide.

### 4.2.1 Effect of oxidants and solvents to oxidation reaction.

Experiment of oxidantion reaction of sulfur compound in high speed diesel in batch reactor to study the effect of oxidants and solvents to oxidation reaction have condition as follows;

Volume of high speed diesel 200ml. (169.9g.)

Volume of solvent 200 ml.

Reaction temperature 90 °C, stirring speed 1600 cycle/min.

Time for adding oxidant 30 min.

Reaction Time 60 min.

Variable for studying this oxidation reaction of sulfur compound in high speed speed diesel are type of oxidant, content of oxidant, type of solvent, concentration of solvent and reaction time of oxidation reaction.

From Table 4.3, increasing content of oxidation 3.0 ml., 5.0 ml. and 8.0 ml. will increase oxidation reaction of sulfur compound. (sulfur content in high speed diesel will decrease.)

Table 4.3 Effect of oxidants and solvents to oxidation reaction.

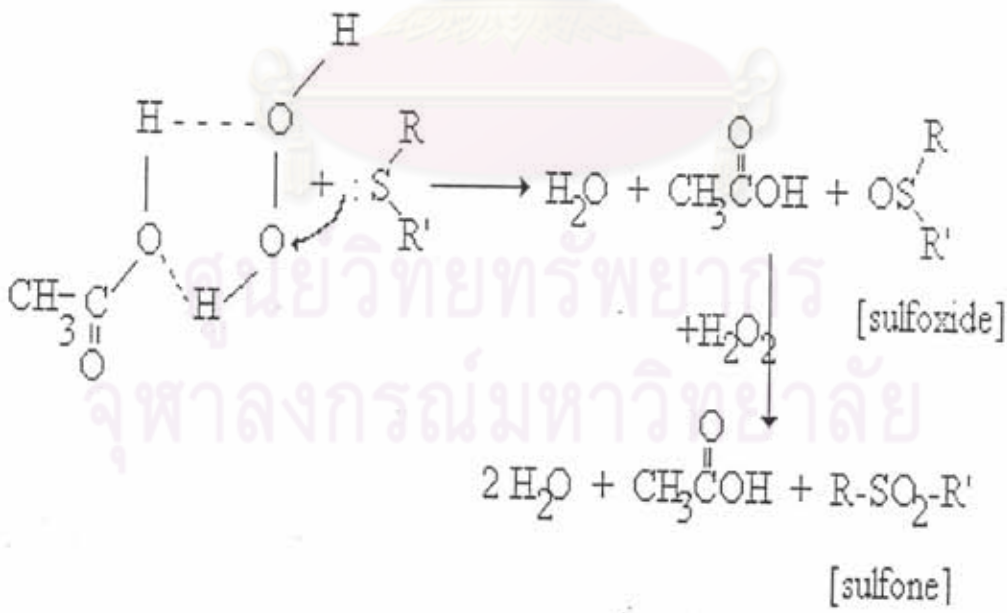
| Experiment | Oxidant. | Solvent | | | | | |
|---|---|---|---|---|---|---|---|
| | | Acetic acid | | | Ethanol | | |
| | | Sulfur content (%wt.) | Colour (ASTM Colour) | Removal sulfur (%wt.) | Sulfur content (%wt.) | Colour (ASTM Colour) | Removal sulfur (%wt.) |
| 1 | tert-butyl hydroperoxide = 3.0 ml.(2.80g.) | 0.52 | 1.0 | 17.46 | 0.62 | L 1.0 | 1.59 |
| 2 | tert-butyl hydroperoxide = 5.0 ml.(4.67g.) | 0.49 | 1.5 | 22.22 | 0.62 | L 1.0 | 1.59 |
| 3 | tert-butyl hydroperoxide = 8.0 ml.(7.46g.) | 0.44 | 2.0 | 30.16 | 0.62 | L 1.0 | 1.59 |
| 4 | hydrogen peroxide = 3.0 ml.(3.37g.) | 0.34 | 1.0 | 46.03 | 0.61 | L 1.0 | 3.17 |
| 5 | hydrogen peroxide = 5.0 ml.(5.62g.) | 0.26 | 1.5 | 58.73 | 0.58 | 1.0 | 7.94 |
| 6 | hydrogen peroxide = 6.0 ml.(6.74g.) | 0.24 | 2.5 | 61.90 | 0.56 | 1.0 | 11.11 |
| 7 | hydrogen peroxide = 8.0 ml.(8.99g.) | 0.18 | 3.5 | 71.43 | 0.52 | 1.0 | 17.46 |

The result 1-3, oxidation reaction of sulfur compound in high speed diesel by tert-butyl hydroperoxide as oxidant can occur fluently by reaction when using acetic acid as solvent. It is easy to see from reducing of sulfur content and increasing of colour of high speed diesel because of oxidized hydrocarbon. But the result 4-7 shows that hydrogen peroxide is better oxidant than tert-butyl hydroperoxide and acetic acid is suitable solvent in oxidation reaction of sulfur compound, which is better than ethanol solvent.

Mechanism of oxidation reaction of sulfur compound in high speed diesel by peroxide oxidant is

$$2H_2O_2 + CH_3COOH + R\text{-}S\text{-}R' \text{ ------> } CH_3COOH + 2H_2O + R\text{-}SO_2\text{-}R'$$

From reaction, one mole of oxidizing agent reacts with one mole of sulfur compound to sulfoxide and two oxidizing agents react with one mole of sulfur compound to sulfone.




RSR' = sulfur compound

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From experiment 4-7, content of hydrogen peroxide effects to oxidation reaction. The more hydrogen peroxide content in oxidation reaction, the more sulfoxide of sulfone in high speed diesel. Because of more polarity forms so high speed diesel is more extractability and hence improves the yield of desulfured raffinate. And these sulfur compounds transfer from hydrocarbon phase to acetic acid phase, as solvent for oxidation reaction. So sulfur content in high speed diesel is reduced.

The mechanism is shown as below;

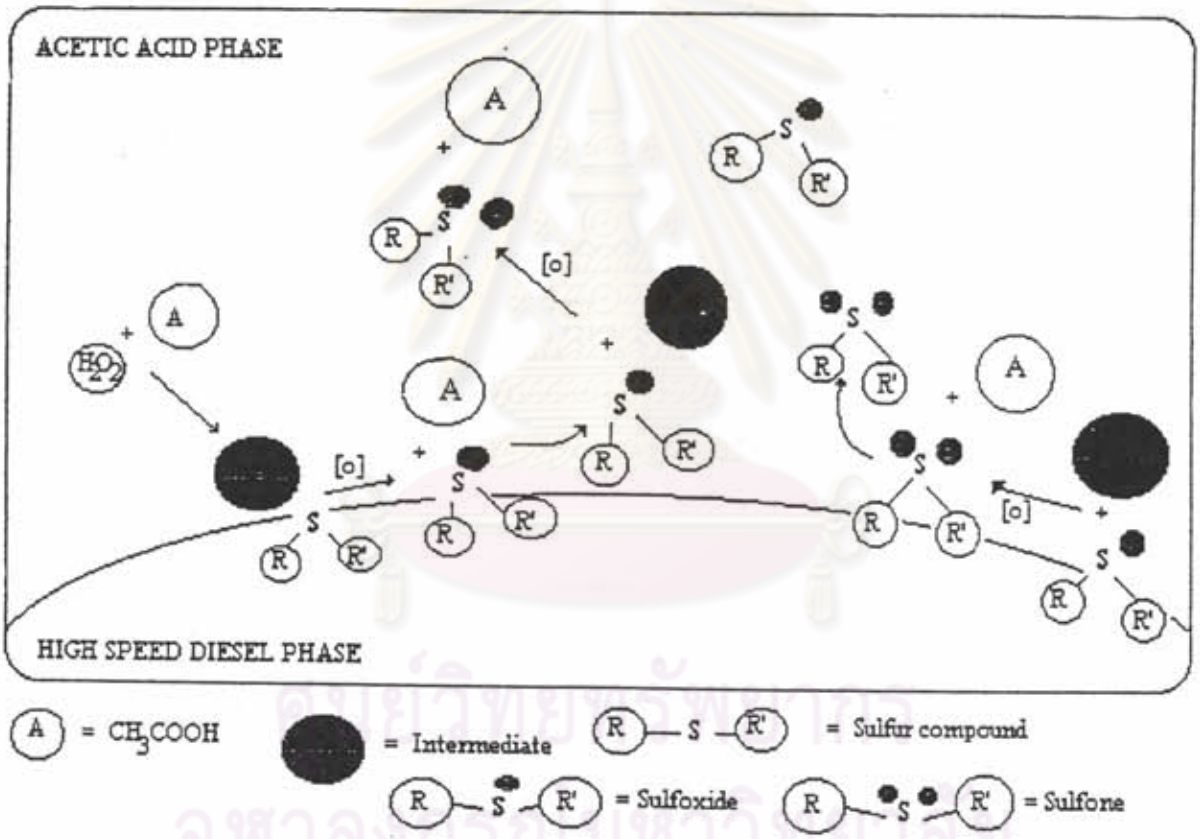


Fig. 4.1 Oxidation reaction with simultaneous extraction.

Fig. 4.1 shows mechanism of oxidation reaction and process of transfering sulfur compound. Free electron of sulfur atom attachs oxygen atom of complex structure between hydrogen peroxide and acetic acid, which is calls sulfoxide.

Sulfoxide gives higher activity than sulfur compound. So sulfoxide can react to be sulfone.

Sulfoxide and sulfone have more polarity than sulfur compound so they will transfer from high speed diesel to acetic acid phase, which decrease sulfur content in high speed diesel.

But using hydrogen peroxide too much, it will occur violent oxidation. And this effects molecule of hydrocarbon to be oxidixed. So colour of high speed diesel is darker. This process is difficult to control so hydrogen peroxide content for oxidation sulfur compound in high speed diesel should be equal to sulfur compound content in high speed diesel.

Examination of the infrared spectra of the high speed diesel which has undergone oxidative desulfurization shows that the characteristic of sulfone peaks at round 1300 $cm^{-1}$ and 1150 $cm^{-1}$ and sulfoxide peaks at round 1050 $cm^{-1}$ in Fig. 4.3.

From the infrared spectra, peak of carbony bond( -C=O ) is shown after oxidation reaction which means that hydrocarbon in high speed diesel is oxidized so colour is darker as in Fig. 4.2. Darker colour of high speed diesel relates to oxidant content in oxidation reaction.


Fig. 4.2 Effect of hydrogen peroxide as oxidant to colour of high speed diesel.

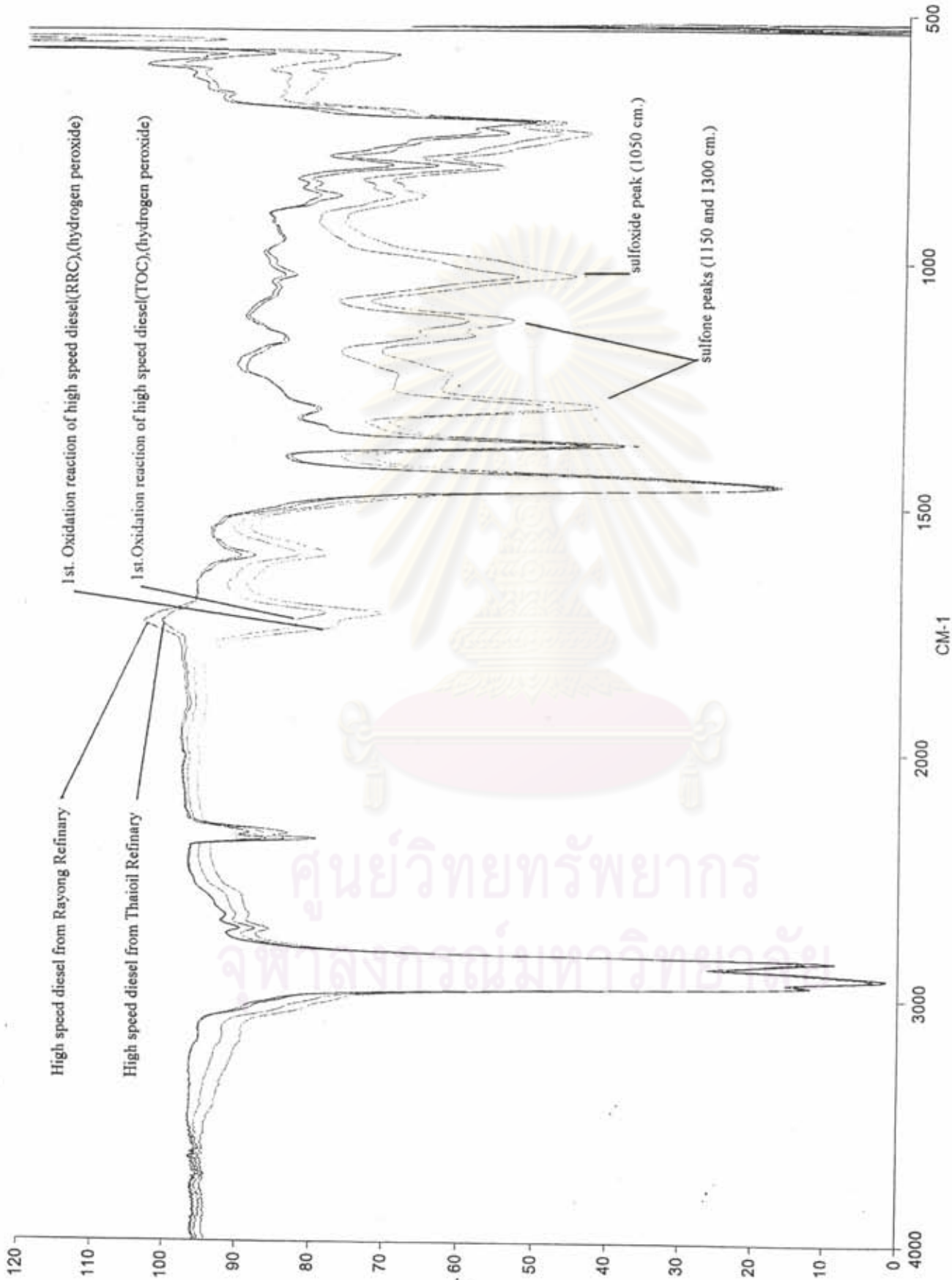


Fig. 4.3 Examination of the infrared spectra of high speed diesel after oxidation reaction.

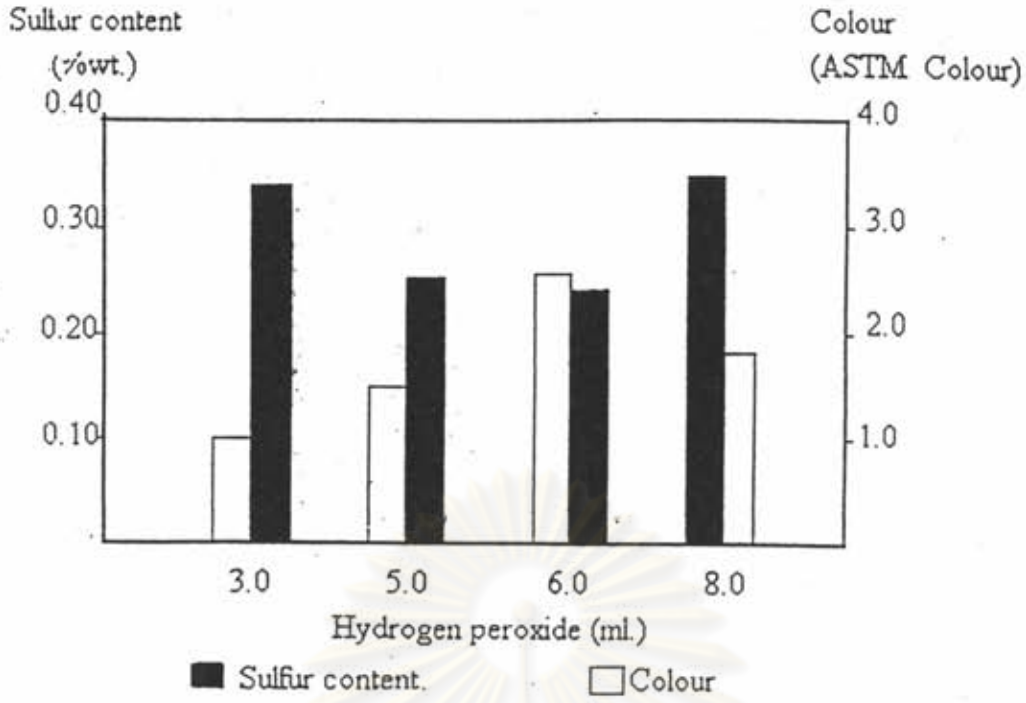


Fig 4.4 Effect of hydrogen peroxide to oxidation reaction.

Report of Amir Attar and William H. Corcoran present that hydrogen peroxide suits to aromatic sulfur compound such as benzyl methyl sulfide and dibenzothiophene. But tert-butyl hydroperoxide is for cyclo sulfur compound such as cyclohexyl methyl sulfide and tert-butyl hydroperoxide which have low active oxygen. For this study, hydrogen peroxide is proper for oxidation reaction of high speed diesel.

Besides that solvent effects to oxidation reaction. And acetic acid is more suitable than ethyl alcohol in oxidation reaction because in the mechanism of oxidation reaction occurs intermediate of oxidant and solvent in six-side ring. H-O bond of solvent is cleaven by free radical of sulfur atom which H-O bond in acetic acid is weaer than in ethylalcohol.

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4.2.2 Result of sulfur content in high speed diesel after oxidation reaction.

Table 4.3 can be concluded that suitable condition for oxidation reaction of sulfur compound in high speed diesel by hydrogen peroxide as oxidant is using cooperative solvent which is acetic acid.

Table 4.4 can present relationship between oxidation reaction and sulfur content and colour of high speed diesel after oxidation reaction as in Fig 4.5. Colour of high speed diesel will be steady at 1.5 (ASTM Colour) because using oxidant agent content equal to sulfur content in high speed diesel protects violent oxidation reaction. Sulfur content in high speed diesel after oxidation reaction can be reduced approximately 50% by weight. At the third oxidation reaction, sulfur content in high speed diesel is about 0.05% by weight.

Table 4.4 Procedure of experiment 8.

Condition: Volume of high speed diesel 200 ml. (169.9g.)

Volume of acetic acid 200 ml. (209.0g.)

Using hydrogen peroxide as oxidant:

the first times = 4.2 g.

the secont times = 2.2 g.

the third times = 0.87 g.

Reaction temperature 90 °C, stirring speed 1600 cycle/min.

Time for adding oxidant 30 min.

Result 8:

| Oxidation reaction | 1st | 2nd | 3th |
|---|---|---|---|
| Sulfur content (%wt.) | 0.33 | 0.13 | 0.05 |
| Colour (ASTM Colour) | 1.5 | 1.5 | 1.5 |
| Removal sulfur (%wt.) | 47.62 | 79.36 | 92.06 |

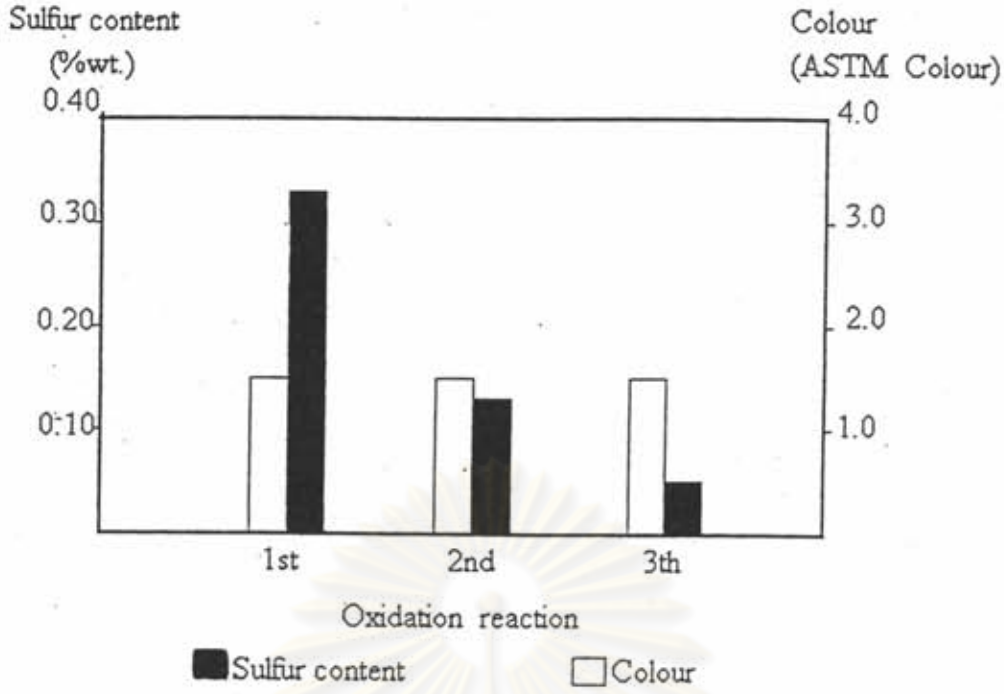



Fig. 4.5 Oxidation reaction.

4.2.3 Effect of acetic acid and reaction time to oxidation reaction.

Effect of acetic acid as solvent in oxidation reaction by change of concentration of acetic acid and recovery acetic acid for reoxidation reaction are studied. Sulfur content and colour are shown in the results. The results of studying effective of hydrogen peroxide quatity as oxidant in oxidation reaction equal to sulfur quatity in high speed diesel are shown in table 4.5-4.7.

From experiment 9-11, the less acetic acid in oxidation reaction, the less intermediate of hydrogen peroxide and acetic acid, the less oxidation reaction of sulfur compound in high speed diesel.

The report of L.I. Belen'kii (1990) shows the activity of oxidation reaction as this, $RSO_2 \approx RSO > SCN > RS > SH$. Sulfone and sulfoxide are found in recovery acetic acid in oxidation reaction when using recovery acetic acid in oxidation reaction, sulfur compound in high speed diesel is reduced. If using the fourth recovery of acetic acid, sulfur compound in high speed diesel will be 0.55 %wt. That means this process reducing sulfur compound 12.70 %wt.

Increasing reaction time of oxidation reaction reduces sulfur content in high speed diesel but effects to darker colour of high speed diesel.

Table 4.5 Procedure of experiment 9.

Condition: Using hydrogen peroxide (4.2g.) as oxidant.
Volume of high speed diesel 200 ml. (169.9g.)
Volume of acetic acid 200 ml. (209.0g.)
Reaction temperature 90 °C, stirring speed 1600 cycle/min.
Time for adding oxidant 30 min.

Result 9:

| Acetic acid concentration (%Vol.) | 40% | 60% | 80% | 100% |
|---|---|---|---|---|
| Sulfur content (%wt.) | 0.54 | 0.47 | 0.44 | 0.33 |
| Removal sulfur (%wt.) | 14.29 | 25.40 | 30.16 | 47.62 |

Table 4.6 Procedure of experiment 10.

Condition: Using hydrogen peroxide (4.2g.) as oxidant.
Volume of high speed diesel 200 ml. (169.9g.)
Volume of acetic acid 200 ml. (209.0g.)
Reaction temperature 90 °C, stirring speed 1600 cycle/min.
Time for adding oxidant 30 min.

Result 10:

| Recycle acetic acid (cycle) | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Sulfur content (%wt.) | 0.33 | 0.39 | 0.49 | 0.55 |
| Colour (ASTM Colour) | 1.5 | 2.5 | 2.5 | 2.5 |
| Removal sulfur (%wt.) | 47.62 | 38.09 | 22.22 | 12.70 |

Table 4.7 Procedure of experiment 11.

Condition: Using hydrogen peroxide (4.2g.) as oxidant.

Volume of high speed diesel 200 ml. (169.9g.)

Volume of acetic acid 200 ml. (209.0g.)

Reaction temperature 90 °C, stirring speed 1600 cycle/min.

Time for adding oxidant 30 min.

Result 11:

| Reaction time of oxidation reaction (min.) | 30 | 60 | 90 |
|---|---|---|---|
| Sulfur content (%wt.) | 0.36 | 0.33 | 0.29 |
| Colour (ASTM Colour) | 1.0 | 1.5 | 2.0 |
| Removal sulfur (%wt.) | 42.86 | 47.62 | 53.97 |

## 4.3 CONDITION OF OXIDATION REACTION USING PEROXY ACID AS OXIDANT.

For investigation suitable condition for oxidation reaction of sulfur compound in high speed diesel by using peroxy acid as oxidant, solvent for this study are acetic acid and methanol. Table 4.8 shows results of the experiments which consist of sulfur content in high speed diesel and its color

There are many kinds of peroxy acid but the one that suits for aromatic sulfur compound is peracetic acid as oxidant for desulfurization of high speed diesel. High speed diesel from Thaioil Refinery having sulfur content about 0.63 % is used to find condition of oxidation reaction using peracetic acid as oxidants.

4.3.1 Effect of peracetic acid and solvent to oxidation reaction.

Experiment of oxidation reaction of sulfur compound in high speed diesel in batch reactor to study the effect of peracetic acid and solvents to oxidation reaction have a condition;

Volume of high speed diesel 200 ml. (169.9g.)

Volume of solvent 200 ml.

Reaction temperature 60°C, stirring speed 1600 cycle/min.

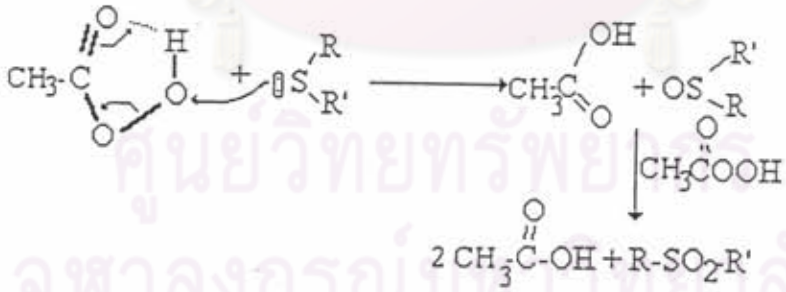
Time for adding oxidant 30 min.

Reaction time 45 min,

Variable for studying oxidation reaction are the content of oxidant and the type of solvent.

The results of oxidation reaction of sulfur compound in high speed diesel by peracetic acid as oxidant, acetic acid and methanol as solvent do not effect to oxidation reaction which mechanism of reaction is presented follow this;

$$CH_3(CO)OOH + R\text{-}S\text{-}R' \text{ --------> } CH_3(CO)OH + R\text{-}SO_2\text{-}R'$$



RSR' = sulfur compound

Table 4.8 Effect of peracetic acid and solvents to oxidation reaction.

| Experiment | Volume of peracetic acid (g.) | Solvent | | | | | |
|---|---|---|---|---|---|---|---|
| | | Acetic acid | | | Methanol | | |
| | | Sulfur content (%wt.) | Colour (ASTM Colour) | Removal sulfur (%wt.) | Sulfur content (%wt.) | Colour (ASTM Colour) | Removal sulfur (%wt.) |
| 12 | 7.5 | 0.52 | L 1.0 | 17.46 | 0.50 | L 1.0 | 20.63 |
| 13 | 10.0 | 0.48 | L 1.0 | 23.81 | 0.48 | L 1.0 | 23.81 |
| 14 | 12.5 | 0.48 | L 1.0 | 23.81 | 0.48 | L 1.0 | 23.81 |
| 15 | 15.0 | 0.48 | L 1.0 | 23.81 | 0.48 | L 1.0 | 23.81 |
| 16 | 17.5 | 0.48 | L 1.0 | 23.81 | 0.47 | L 1.0 | 25.40 |

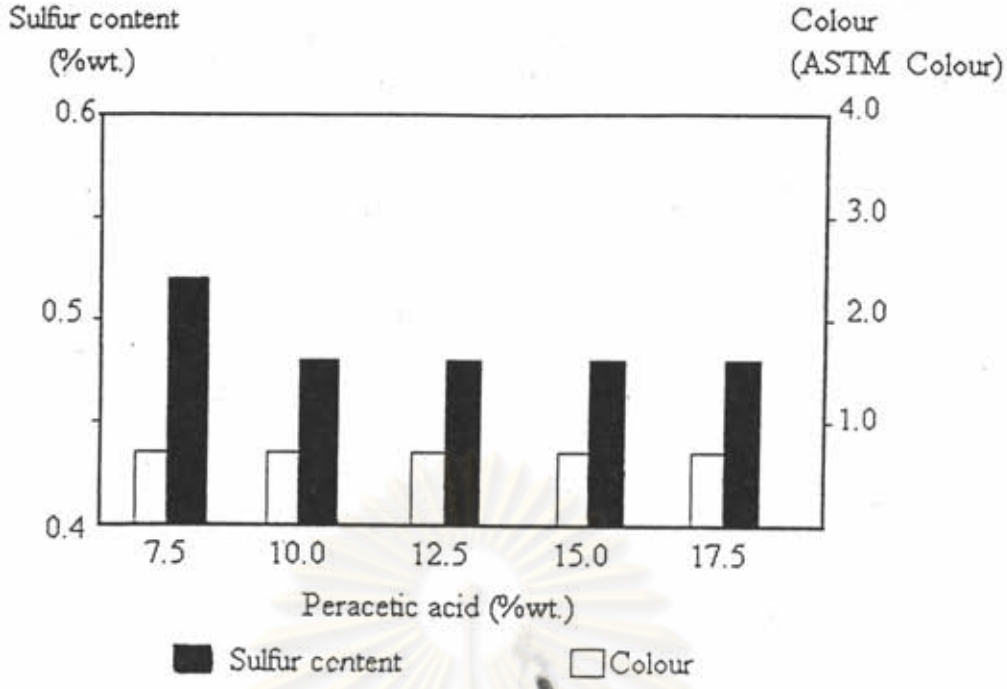



Fig. 4.6 Effect of peracetic acid to oxidation reaction.

Increasing peracetic acid makes sulfur compound occur reaction resulting in decreasing sulfur content. Sulfur content will be only decreased to 0.48% although the content peracetic acid is increased.

Peracetic acid as oxidant behaves as intermediate by itself and that system can reduce sulfur content to 0.48% by wt. because peracetic acid is not stable, it can occur reversible reaction to acetic acid as below.

$$CH_3COOH + H_2O_2 \rightleftharpoons CH_3(CO)OOH + H_2O$$

So peracetic acid is not suitable oxidant for oxidation reaction of sulfur compound in high speed diesel.

## 4.4 EXPERIMENT OF OXIDATION REACTION USING HYDROGEN PEROXIDE AS OXIDANT.

Experiment 4.1, suitable condition for oxidation reaction of sulfur content in high speed diesel by acetic acid as solvent is using hydrogen peroxide content equal to sulfur content in high speed diesel, reaction temperature 90°C, time of adding oxidant 30 minutes and setting 60 minutes for reaction.

Studied oil in this thesis is taken from Thaioil Refinary and Rayong Refinary. Physical properties of high speed diesel after desulfurization by oxidation reaction are considered. Those are shown the testing items in Table 4.9-4.10. For the original physical properties are shown in Table 4.1.

From the results, sulfur content in high speed diesel can be reduced to less than 0.25 %wt. Some physical properties of high speed diesel are effected because reducing aromatic content effects to increasing pour points. Other properties such as flash point, density, viscosity, colour and distillation are not changed so much.

## 4.5 EXPERIMENT OF OXIDATION REACTION USING PEROXY ACID AS OXIDANT.

Experiment 4.3, suitable condition for oxidation reaction of sulfur content in high speed diesel by acetic acid as solvent is using peracetic acid content equal to sulfur content in high speed diesel, reaction temperature 60°C, time of adding oxidant 30 minutes and setting 60 minutes for reaction.

Studied oil in this thesis is taken from Thaioil Refinary and Rayong Refinary. Physical properties of high speed diesel after desulfurization by oxidation reaction are considered. Those are shown the testing items in Table 4.11. The original physical properties are shown in Table 4.1.

Table 4.9 The physical properties of high speed diesel after the first oxidation reaction by hydrogen peroxide.

| Physical property | Test method | High speed diesel (Thaioil Refinary) | High speed diesel (Rayong Refinary) |
|---|---|---|---|
| Density @15 °C (kg/l.) | ASTM D-1298 | 0.8506 | 0.8505 |
| Viscosity @40 °C (cst.) | ASTM D-445 | 4.49 | 5.88 |
| Flash Point,PMCC (°C. ) | ASTM D-93 | 102 | 98 |
| Pour point (°C. ) | ASTM D-97 | 3.0 | 6.0 |
| Colour (ASTM Colour) | ASTM D-1500 | 1.5 | L 1.5 |
| Sulfur Content (%wt.) | ASTM D-4294 | 0.32 | 0.43 |
| Removal sulfur (%wt.) | - | 49.21 | 53.26 |
| Aromatic content (%wt.) | ASTM D-1319 | 10.02 | 20.97 |
| Distillation (°C. ) | ASTM D-86 | | |
| IBP | | 222.5 | 243.1 |
| 10% | | 258.4 | 285.1 |
| 50% | | 300.1 | 329.4 |
| 90% | | 362.9 | 356.7 |
| End Point | | 380.6 | 368.2 |
| Yield (%wt.) | - | 87.4 | 83.5 |

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Table 4.10 The physical properties of high speed diesel after the second oxidation reaction by hydrogen peroxide.

| Physical property | Test method | High speed diesel (Thaioil Refinary) | High speed diesel (Rayong Refinary) |
|---|---|---|---|
| Density @15 °C (kg/l.) | ASTM D-1298 | 0.8403 | 0.8408 |
| Viscosity @40 °C (cst.) | ASTM D-445 | 4.57 | 5.94 |
| Flash Point,PMCC (°C. ) | ASTM D-93 | 100 | 98 |
| Pour point (°C. ) | ASTM D-97 | 6.0 | 9.0 |
| Colour (ASTM Colour) | ASTM D-1500 | 1.5 | L 1.5 |
| Sulfur Content (%wt.) | ASTM D-4294 | 0.16 | 0.22 |
| Removal sulfur (%wt.) | - | 50.0 | 48.84 |
| Aromatic content (%wt.) | ASTM D-1319 | 7.69 | 17.42 |
| Distillation (°C. ) | ASTM D-86 | | |
| IBP | | 224.6 | 247.6 |
| 10% | | 260.2 | 287.6 |
| 50% | | 302.9 | 326.5 |
| 90% | | 365.7 | 360.4 |
| End Point | | 383.9 | 373.8 |
| Yield (%wt.) | - | 86.8 | 84.1 |

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Table 4.11 The physical properties of high speed diesel after oxidation using peracetic acid as oxidant.

| Physical property | Test method | High speed diesel (Thaioil Refinary) | High speed diesel (Rayong Refinary) |
|---|---|---|---|
| Density @15 °C (kg/l.) | ASTM D-1298 | 0.8542 | 0.8501 |
| Viscosity @40 °C (cst.) | ASTM D-445 | 4.48 | 5.87 |
| Flash Point,PMCC (°C. ) | ASTM D-93 | 100 | 98 |
| Pour point (°C. ) | ASTM D-97 | 0.0 | 3.0 |
| Colour (ASTM Colour) | ASTM D-1500 | L 1.0 | 0.5 |
| Sulfur Content (%wt.) | ASTM D-4294 | 0.49 | 0.71 |
| Removal sulfur (%wt.) | - | 22.22 | 22.83 |
| Aromatic content (%wt.) | ASTM D-1319 | 12.42 | 22.96 |
| Distillation (°C. ) | ASTM D-86 | | |
| IBP | | 220.7 | 242.8 |
| 10% | | 253.4 | 281.3 |
| 50% | | 298.5 | 325.1 |
| 90% | | 363.6 | 359.9 |
| End Point | | 387.9 | 367.2 |
| Yield (%wt.) | - | 88.9 | 86.5 |

Hydrogen peroxide as oxidant, one of hydroperoxide oxidants, can be intermediate with acetic acid in oxidation reaction of sulfur compound. Sulfur compound after oxidation reaction becomes sulfone and sulfoxide forms which show the characteristic of sulfone and sulfoxide peaks as in Fig. 4.3. Sulfone and sulfoxide forms are high polarity and can transfer to acetic acid layer. Which cause lower sulfur content in high speed diesel approximately 50% by wt. in first oxidation, 75% by wt. in second oxidation. Peracetic acid as oxidant can make sulfur compound to be

oxidized but peracetic acid is not stable structure. So sulfur content is removal only to 22.5% by wt.

## 4.6 SOLVENT EXTRACTION

Experiment for extraction sulfur compound by solvents; methanol, acetic acid, ethanolamine and ammonia has been studied.

Mixing solvent with high speed diesel in ratio 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 3.00 and 4.00 in separatory funnel. Then shake at room temperature. The results in Table 4.12, 4.13, 4.14 and 4.15 consist of sulfur content and compare efficiency of solvents.

In experiment of solvent extraction by solvent two groups, Group A; methanol, acetic acid, Group B; ethanolamine, ammonia. Group B has less polarity than group A because of oxygen atom. From results, solvent in group A has extractability more than group B. And methanol gives the most efficiency.

Part I of experiment shows that acetic acid is suitable solvent for oxidation reaction by hydrogen peroxide. Part II, acetic acid in oxidation reaction not only extracts but also reacts oxidation so sulfur content (%wt.) in high speed diesel decrease after oxidation reaction. We can conclude that desulfurization by solvent extraction does not complete because sulfur compound in sulfoxide and sulfone forms are extracted after oxidation process.

Table 4.12 Result of using ammonia as solvent in solvent extraction.

| Ratio. Solvent : Gas oil (g.) | Sulfur content (%wt.) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Hydrogen peroxide as oxidant | | | | | | | | Peracetic acid as oxidant | | | |
| | TOC 1st(0.32%S) | | TOC 2nd(0.16%S) | | RRC 1st(0.43%S) | | RRC 2nd(0.22%S) | | TOC (0.49%S) | | RRC (0.71%S) | |
| | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) |
| 0.25 | 0.32 | 98.4 | 0.15 | 98.8 | 0.42 | 98.1 | 0.21 | 98.8 | 0.49 | 98.7 | 0.70 | 98.0 |
| 0.50 | 0.31 | 97.2 | 0.14 | 97.9 | 0.42 | 97.5 | 0.20 | 97.5 | 0.48 | 97.8 | 0.70 | 97.1 |
| 0.75 | 0.30 | 96.3 | 0.14 | 96.4 | 0.41 | 96.7 | 0.20 | 96.8 | 0.46 | 96.5 | 0.68 | 96.1 |
| 1.00 | 0.28 | 95.8 | 0.12 | 96.0 | 0.40 | 96.3 | 0.19 | 95.4 | 0.45 | 96.0 | 0.66 | 95.3 |
| 1.50 | 0.28 | 94.1 | 0.10 | 94.7 | 0.38 | 94.2 | 0.18 | 94.2 | 0.44 | 94.7 | 0.66 | 94.3 |
| 2.00 | 0.27 | 93.4 | 0.10 | 93.9 | 0.36 | 93.0 | 0.18 | 93.1 | 0.44 | 93.0 | 0.66 | 93.6 |
| 3.00 | 0.27 | 92.8 | 0.10 | 93.2 | 0.36 | 92.6 | 0.18 | 92.5 | 0.44 | 91.9 | 0.66 | 92.5 |
| 4.00 | 0.27 | 92.1 | 0.10 | 92.5 | 0.36 | 91.9 | 0.18 | 92.4 | 0.44 | 91.7 | 0.66 | 91.4 |

TOC 1st (#.##%S) = The 1st. oxidation reaction of high speed diesel from Thaioil Refinary (sulfur content,%wt.)

TOC 2nd. (#.##%S) = The 2nd. oxidation reaction of high speed diesel from Thaioil Refinary (sulfur content,%wt.)

RRC 1st (#.##%S) = The 1st. oxidation reaction of high speed diesel from Rayong Refinary (sulfur content,%wt.)

RRC 2nd. (#.##%S) = The 2nd. oxidation reaction of high speed diesel from Rayong Refinary (sulfur content,%wt.)

Table 4.13 Result of using ethanolamine as solvent in solvent extraction.

| Ratio. Solvent : Gas oil (g.) | Sulfur content (%wt.) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Hydrogen peroxide as oxidant | | | | | | | | Peracetic acid as oxidant | | | |
| | TOC 1st(0.32%S) | | TOC 2nd(0.16%S) | | RRC 1st(0.43%S) | | RRC 2nd(0.22%S) | | TOC (0.49%S) | | RRC (0.71%S) | |
| | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) |
| 0.25 | 0.31 | 89.1 | 0.14 | 89.0 | 0.42 | 89.3 | 0.20 | 89.6 | 0.48 | 89.2 | 0.70 | 89.0 |
| 0.50 | 0.30 | 88.2 | 0.15 | 88.1 | 0.41 | 87.9 | 0.19 | 88.5 | 0.47 | 88.2 | 0.69 | 88.4 |
| 0.75 | 0.29 | 87.7 | 0.13 | 87.5 | 0.39 | 87.1 | 0.18 | 87.6 | 0.45 | 87.8 | 0.68 | 87.5 |
| 1.00 | 0.27 | 85.4 | 0.13 | 85.6 | 0.37 | 85.2 | 0.16 | 85.4 | 0.42 | 85.3 | 0.66 | 85.9 |
| 1.50 | 0.25 | 86.2 | 0.12 | 86.3 | 0.35 | 86.1 | 0.14 | 86.1 | 0.41 | 86.4 | 0.63 | 86.3 |
| 2.00 | 0.23 | 84.6 | 0.10 | 84.1 | 0.33 | 84.4 | 0.12 | 84.7 | 0.38 | 84.8 | 0.62 | 84.2 |
| 3.00 | 0.22 | 82.9 | 0.08 | 82.7 | 0.33 | 82.5 | 0.10 | 82.7 | 0.36 | 82.8 | 0.62 | 82.5 |
| 4.00 | 0.22 | 81.1 | 0.08 | 81.0 | 0.33 | 81.2 | 0.10 | 81.5 | 0.34 | 81.7 | 0.61 | 81.4 |

TOC 1st (#.##%S) = The 1st. oxidation reaction of high speed diesel from Thaioil Refinary (sulfur content,%wt.)

TOC 2nd. (#.##%S) = The 2nd. oxidation reaction of high speed diesel from Thaioil Refinary (sulfur content,%wt.)

RRC 1st (#.##%S) = The 1st. oxidation reaction of high speed diesel from Rayong Refinary (sulfur content,%wt.)

RRC 2nd. (#.##%S) = The 2nd. oxidation reaction of high speed diesel from Rayong Refinary (sulfur content,%wt.)

Table 4.14 Result of using acetic acid as solvent in solvent extraction.

| Ratio. Solvent : Gas oil (g.) | Sulfur content (%wt.) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Hydrogen peroxide as oxidant | | | | | | | | Peracetic acid as oxidant | | | |
| | TOC 1st(0.32%S) | | TOC 2nd(0.16%S) | | RRC 1st(0.43%S) | | RRC 2nd(0.22%S) | | TOC (0.49%S) | | RRC (0.71%S) | |
| | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) |
| 0.25 | 0.28 | 90.5 | 0.11 | 91.1 | 0.39 | 92.0 | 0.16 | 90.6 | 0.46 | 90.2 | 0.69 | 90.1 |
| 0.50 | 0.27 | 89.8 | 0.10 | 90.4 | 0.38 | 89.7 | 0.15 | 89.5 | 0.45 | 89.6 | 0.68 | 89.8 |
| 0.75 | 0.26 | 89.1 | 0.10 | 89.7 | 0.37 | 89.6 | 0.15 | 89.4 | 0.43 | 88.8 | 0.66 | 89.5 |
| 1.00 | 0.24 | 87.4 | 0.10 | 87.8 | 0.36 | 86.9 | 0.14 | 87.1 | 0.40 | 87.3 | 0.64 | 86.6 |
| 1.50 | 0.21 | 85.2 | 0.09 | 86.2 | 0.34 | 85.8 | 0.12 | 86.5 | 0.37 | 85.9 | 0.62 | 86.1 |
| 2.00 | 0.18 | 81.6 | 0.09 | 82.5 | 0.31 | 82.8 | 0.12 | 82.2 | 0.35 | 82.8 | 0.60 | 82.0 |
| 3.00 | 0.18 | 79.7 | 0.08 | 80.1 | 0.31 | 80.1 | 0.12 | 80.2 | 0.35 | 80.6 | 0.60 | 80.1 |
| 4.00 | 0.17 | 76.1 | 0.08 | 77.2 | 0.31 | 78.4 | 0.12 | 76.8 | 0.34 | 78.5 | 0.60 | 77.5 |

TOC 1st (#.##%S) = The 1st. oxidation reaction of high speed diesel from Thaioil Refinary (sulfur content,%wt.)

TOC 2nd. (#.##%S) = The 2nd. oxidation reaction of high speed diesel from Thaioil Refinary (sulfur content,%wt.)

RRC 1st (#.##%S) = The 1st. oxidation reaction of high speed diesel from Rayong Refinary (sulfur content,%wt.)

RRC 2nd. (#.##%S) = The 2nd. oxidation reaction of high speed diesel from Rayong Refinary (sulfur content,%wt.)

Table 4.15 Result of using methanol as solvent in solvent extraction.

| Ratio. Solvent : Gas oil (g.) | Sulfur content (%wt.) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Hydrogen peroxide as oxidant | | | | | | | | Peracetic acid as oxidant | | | |
| | TOC 1st(0.32%S) | | TOC 2nd(0.16%S) | | RRC 1st(0.43%S) | | RRC 2nd(0.22%S) | | TOC (0.49%S) | | RRC (0.71%S) | |
| | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) | %S | Yield (%) |
| 0.25 | 0.30 | 98.8 | 0.13 | 99.1 | 0.40 | 98.7 | 0.18 | 99.3 | 0.47 | 98.5 | 0.70 | 99.2 |
| 0.50 | 0.28 | 96.7 | 0.13 | 96.9 | 0.39 | 96.8 | 0.17 | 96.9 | 0.46 | 96.8 | 0.70 | 97.0 |
| 0.75 | 0.27 | 96.1 | 0.12 | 96.4 | 0.38 | 95.9 | 0.16 | 96.1 | 0.45 | 95.9 | 0.69 | 96.8 |
| 1.00 | 0.24 | 95.4 | 0.10 | 95.9 | 0.37 | 95.6 | 0.15 | 95.6 | 0.41 | 95.7 | 0.67 | 96.1 |
| 1.50 | 0.23 | 94.8 | 0.08 | 95.0 | 0.35 | 94.8 | 0.12 | 94.8 | 0.37 | 94.6 | 0.65 | 95.1 |
| 2.00 | 0.22 | 94.2 | 0.07 | 94.5 | 0.32 | 94.5 | 0.10 | 94.3 | 0.35 | 94.3 | 0.63 | 94.8 |
| 3.00 | 0.20 | 93.7 | 0.05 | 93.8 | 0.30 | 93.9 | 0.05 | 92.9 | 0.32 | 93.7 | 0.61 | 94.0 |
| 4.00 | 0.20 | 92.3 | 0.05 | 92.6 | 0.30 | 92.5 | 0.05 | 92.4 | 0.30 | 92.8 | 0.60 | 93.1 |

TOC 1st (#.##%S) = The 1st. oxidation reaction of high speed diesel from Thaioil Refinary (sulfur content,%wt.)

TOC 2nd. (#.##%S) = The 2nd. oxidation reaction of high speed diesel from Thaioil Refinary (sulfur content,%wt.)

RRC 1st (#.##%S) = The 1st. oxidation reaction of high speed diesel from Rayong Refinary (sulfur content,%wt.)

RRC 2nd. (#.##%S) = The 2nd. oxidation reaction of high speed diesel from Rayong Refinary (sulfur content,%wt.)

## 4.7 MODEL OF DESULFURIZATION PROCESS BY OXIDATION WITH SIMULTANEOUS EXTRACTION.

From the experiment, the main removal sulfur compound in high speed diesel is oxidation reaction with simultaneous extraction. Resulting sulfone and sulfoxide transfer to acetic acid layer. So this model is designed to desulfurization process by oxidation with simultaneous extraction process. From Table 4.10, this process can be reduced sulfur compound in high speed diesel to under the standard level (sulfur content 0.25%wt.) by two times of oxidation reaction. This model is useful for support in desulfurization process (HDS).

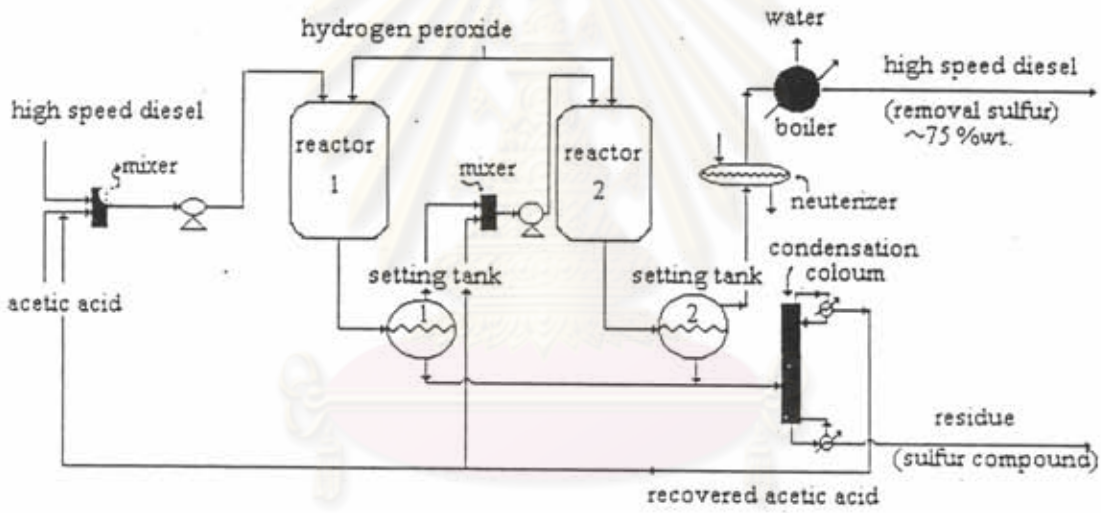


Fig. 4.7 Model of desulfurization process by oxidation with simultaneous extraction.

In this model, high speed diesel is mixed with acetic acid in ratio 1:1 and then passes through tubular reactor. There is unit for adding hydrogen peroxide in oxidation reaction within 30 minutes. And set 60 minutes for the first oxidation reaction. After that solution will separate two layers in setting tank. After that transfer upper which is high speed diesel to second oxidation reaction. We can recover the extract ( acetic acid ) by distillation at temperature about 120°C. High speed diesel from second oxidation will be neuterized which can be removed sulfur content about 75% by wt.