Reducing of SOx Emissions Participates in Decreasing Environmental Pollution

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الخلاصـــــه

الاهتمامات البيئية ادت الى الحاجة الى ازالة المركبات الحاوية على الكبريت من وقود الديزل لخفض انبعاث غازات الاكاسيد المختلفة للكبريت الذي يساهم في خفض التلوث البيئي والامطار الحامضية .

في الاونه الاخيره انصب اهتمام كبير على ازالة الكبريت من وقود الديزيل و الزيوت الخفيفة بطريقة الاكسدة كونها تجري في ظروف تفاعل معتدله.

في هذا البحث تم استقصاء ازالة الكبريت من وقود الديزل بطريقة الاكسدة بالمواد الكيميائية للمر كبات الحاوية على الكبريت عن طريق مركب بيروكسيد الهيدروجين بوجود عامل مساعد مثل حامض الفورميك يتبع ذلك استخلاص المواد المتأكسدة بمذيبات عضويه مثل الاسيتونايترايل او ثنائي مثيل فورمامايد .

لقد وجد ان ازالة الكبريت من وقود الديزل بطريقة الاكسدة هي طريقة واعدة جدا لازالة 85 الى 90% من الكبريت الموجود في الوقود بدرجة حرارة واطئة (25 – 50 م^{0}) و ضغط جوي واحد.

لقد وجد ان التفاعل باعث للحرارة كما ان الحرارة المنبعثة من التفاعل حافظت على استمرار التفاعل في درجة حرارة اعلى من درجة حرارة الغرفة خلال فترة التفاعل لذلك لا تحتاج المواد المتفاعله للتسخين . كذلك وجد ان درجة حرارة الاتقاد تنخفض اضافة الى تأثر طفيف في بعض الخواص الفيزيائيه و الكيميائيه عند تكرار استخلاص المواد المتأكسدة في الوقود بالمذيبات العضوية. ان تكرار عملية الاستخلاص تؤدي الى ازالة بعضا من الهيدركربونات الاروماتيه مما يؤدي الى التأثير على الناتج.

جرى استقصاء استخلاص المركبات الحاوية على الكبريت من وقود الديزل بدون استخدام المواد المؤكسدة بواسطة بعض المذيبات العضويه مثل الداي مثيلفورممايد, الكحول المثيلي, الكحول الاثيلي , ثنائي اثيل ايثر, اسيتايل كلورايد, اسيتونايترايل اضافة الى بعض المذيبات العضويه الاخرى .نتيجة البحث بينت ان افضل مذيب مستخدم لاستخلاص مركبات الكبريت هو ثنائي مثيل فورمامايد.

في هذه الدراسة تم تعديل عملية الاكسدة من خلال تعريض المواد المتفاعلة الى الاشعه فوق البنفسجيه من اجل تحسين ظروف التفاعل .هذه المنظومه الجديدة احتاجت الى كميه اقل من العامل المؤكسد و الطاقة اللازمة لاستكمال التفاعل عند مقارنتها بالطرق السابقة بدون تأثير معتبر على كفائة عملية ازالة الكبريت او نوعية الوقود .

هذه الدراسة توصي باستخدام تقنية الاكسدة و الاستخلاص لتأمين المتطلبات المستقبلية للقوانين التي تحدد نسبة الكبريت في بيئة اقليم كوردستان شمال العراق.

الكلمات المفتاحيه (الرئيسيه): ازالة الكبريت , وقود الديزل , الاشعه فوق البنفسجيه و المرئيه , حامض الفورميك , بيروكسيد الهيدروجين , ازالة الكبريت بالأكسده

Abstract

Environmental concerns have driven the need to remove sulphur-containing compounds from diesel fuel for reducing of SOx emissions which participates in decreasing environmental pollution and acid rain. As the oxidative desulphurization is conducted under very mild reaction conditions, much attention has been recently devoted to this process.

In this contribution, desulphurization of peroxide in the presence of an acid catalyst such as formic acid, followed by extraction of the diesel fuels has been investigated by chemical oxidation of sulphur containing compounds with hydrogen oxidized compounds using acetonitrile or dimethylformamide (DMF). Oxidative desulphurization (ODS) of diesel fuel was found to be very promising approach for the reduction of up to 85 to 90 % of sulphur content at low temperature (25-50 ^{0}C) and atmospheric pressure. The reaction found to be exothermic so, the heat liberated during the reaction maintained continuity of the reaction at higher than room temperature through reaction period, therefore no need to further heating. The flash point of the fuel was decreased and other physical and chemical properties were affected as number of oxidized fuel extraction is repeated. Such extraction also removed sum of other aromatic hydrocarbons and affected the yield.

Extraction of sulphur compound in diesel fuel without oxidation by DMF, alcohol, ethyl alcohol, diethyl ether, acetyl chloride, acetonitrile and other organic solvents were investigated. The investigation showed that the best solvent for sulphur content compound extraction was DMF.

In this study, modifications of the oxidation process occurred including the application of UV. radiation to improve the oxidation process as conducted. The new system required less oxidant and energy as compared to previous generations of desulphurization process without the significant loss of desulphurization efficiency and minimum impact on the fuel quality.

This study recommends that the oxidation extraction technique be used to meet the future environmental sulphur regulations in Kurdistan region north of Iraq

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Keywords: Desulphurization; Diesel Fuel; UV. Visible; Formic acid; Hydrogen peroxide; Oxidative Desulfurization

Introduction

Pollution is an undesirable change in the physical, chemical or biological characteristics of our air, land and water that can harmfully affect human life or that of other species, our industrial processes, living conditions and cultural assets.

Liquid fuels are the main polluter of our atmosphere, they contain a large variety of sulphur compounds (thiols, sulphides, disulphides and thiophenes), which generate SOx and airborne particulate emissions during combustion. [1] Therefore, desulphurization of diesel fuel is extremely important in the petroleum-processing in order to meet worldwide stringent environmental regulations to limit the sulphur levels in transportation fuels.

Sulphur in oil exists in two main forms: The first is termed as active sulphur which can react with metal directly. The second is inactive sulphur which cannot directly react with the metal. Active sulphur includes sulphur, hydrogen sulphide and mercaptan; non-activity includes sulphide, carbon disulphide, thiophenes, and so on. It is found that sulphur in fluid catalytic cracking gasoline , more than 90% sulphur exists in the form of thiophene and its derivatives, while in diesel, thiophene sulphur accounted for 80% of the total sulphur, and benzothiophene and di-benzothiophene accounted for more than 70% of thiophene category [2]

At present, oil desulphurization technology can be broadly divided into two categories: Hydrodesulphurization (HDS) and non-HDS (NHDS), HDS is a kind of technology. We can get H_2S when hydrogen adsorbed on catalyst at high temperature and high pressure reacts with sulphur to remove sulphur. HDS is one kind of more mature technology, but there several shortcomings such as a one-time investment, high running costs and needing a lot of hydrogen, all these increased the cost of diesel fuel significantly. Non-HDS technology does not use hydrogen source and is in line with the requirements of deep desulphurization, so researchers will focus on non-HDS technology. In the last decade, oxidative desulphurization (ODS) has been studied much. [3]

In the conventional catalytic hydrodesulphurization (HDS) process, aliphatic and acyclic thiols, sulphides, and disulphides, are easily removed. However, the removal of sulphur-containing compounds, such as dibenzothiophene (DBT) and its derivatives especially 4,6-dimethydibenzothiophene (4,6-DMDBT), are the key substances that need to be separated from diesel fuel and fuel oil which requires severe operating conditions such as high temperatures, high pressures and high hydrogen consumption, which leads to high capital investment and operational costs.[4]

There are many research and development efforts both on the conventional hydrodesulphurization and on alternative methods such as Adsorptive Desulphurization (ADS) , Biodesulphurization (BDS), Oxidative Desulphurization (ODS) etc. for removing sulphur from diesel fuel. [5]

Oxidative desulphurization (ODS) has been given much attention as an alternative technology for deep desulphurization. The ODS is basically a two-stage process, oxidation, followed by liquid extraction. In the ODS process, the sulphur-containing compounds are oxidized using appropriate oxidants to convert these compounds to their corresponding sulphoxides and sulphones. These are preferentially extracted from light oil due to their increased relative polarity**.**[6,7,8,9] Any unused oxidant that remains in the light oil can be removed by water washing and extracting. The oxidized compounds can be extracted from the light oil by using a non-miscible solvent.

Depending on the solvents used for extraction, the oxidized compounds and solvent are separated from the light oil by gravity separation or centrifugation. The diesel fuel is water washed to recover any traces of dissolved extraction solvent and polished using other methods, such as absorption using silica gel and aluminum oxide. The solvent is separated from the mixture of solvent and oxidized compounds by a simple distillation for recycling and re-use. [5]

Many oxidizing agents have been reported in ODS process, and H_2O_2 is the main one. After the desulphurization reaction, H_2O_2 decompose to H_2O and O_2, so there is no secondary pollution, and meanwhile oxygen is a kind of favorable oxidant. Proper quantities catalysts can accelerate reaction and increase oxidation efficiency. [3]

More recently the removal of organic-sulphur compounds by adsorption desulphurization process was proposed and examined. The adsorption by activated carbon caused reduction in sulphur content by more than 54% of the original sulphur content value while carbonized date palm kernel powder without any activation process showed lower performance toward sulphur recovery. [10] An efficient mild desulphurization process will provide several benefits. It lowers the final fuel price, economizes the desulphurization energy consumption and produces lower amounts of pollutants. [1]

The aim of present study is for put forward a less cost, more efficient novel method for desulphurizing diesel fuel which participates in reducing environment pollution.

Materials and Methods

a- Untreated sample of diesel fuel with sulphur content in the range of 1100-1200 ppm were purchased at retail outlets and placed in 25 liter polyethylene container.

b- All reagents and solvents used were available commercially and were used without further purification unless indicated otherwise.

c- UV tube

Specifications: 2 Pins each end cap/base type, germicidal clear colour, 25 mm diameter, 570 mm length, power output 20 watts, 253.5 nm wavelength was used

d- X-ray sulfur-in-oil analyzer meter model RX-360SH, TANAKA Company. Japan

Specifications**:** RX-360SH determines total sulphur in diesel fuel using energy dispersive X-ray fluorescence (EDXRF) method, which is an accurate, non-destructive, economical and yet quick method in accordance with ISO 8754 and ASTM D4294-03.

Experimental method

1- Solvent extraction on diesel fuel without oxidative treatment

Solvent extraction studies for the removal of sulphur compounds in untreated diesel fuel were investigated with more than six different organic solvents of different polarities, such as dimethylformamide (DMF), methyl alcohol, ethyl alcohol, diethyl ether, acetyl chloride, acetonitrile and other organic solvents. A 20.0 mL of untreated diesel were mixed with the known 3mL of polar organic solvents to determine the efficiency of solvent extraction. The diesel–solvent mixture was stirred for 2 minutes before separating the two layers. It was observed that longer time of stirring cause colloidal mixture difficult to separate in layers. After extraction by the respective polar solvents, the total sulphur content in the sulphur content compound in the diesel was measured by sulphur-in-oil analyzer model (RX-360SH)

The investigation showed that the best polar solvent for sulphur content compound extraction was dimethylformamide. This is in accordance with previous finding [11]

2- Catalytic oxidation followed by solvent extraction on diesel fuel

Different volumes of diesel fuel were treated with different mixtures containing 98% formic acid and 30% hydrogen peroxide. The mixtures were mixed immediately each time before adding them to the diesel fuel. The formic acid was used as catalysts. The oxidation reactions were carried out with 300.0 mL of diesel fuel in a 500mL conical flask at a temperature range of 25–50 ^{0}C, during the time of the reaction which last for about 120 minutes, the reaction mixture was stirred and exposed to U.V. light (253.5 nm wavelength) throughout the reaction period. It was observed that the reaction is exothermic and the temperature was risen throughout the reaction period more than 50 ^{0}C.The heat of the reaction was maintained the oxidation to proceed at higher than room temperature. The colour of the diesel was changed to pale yellow and a layer of tar like was observed at the bottom of the flask.

The treated diesel fuel was separate, by gravity separation, from aqueous and tar like layers which deposed beneath aqueous layer.

The 300mL separated diesel layer was divided in two 150 mL, in order to secure the reaction conditions for both extraction either by DMF or acetonitrile. 150 mL diesel was shacked in separating funnel for 1-2 minutes with 20 mL of either DMF or acetonitrile for extraction. The mixture was left for 3 to 4 hours to separate the diesel layer. The diesel fuel then washed with water to recover any traces of dissolved extraction solvent and polished using silica gel.

The separated diesel layer in each extraction was washed with excess tap water, dried on silica gel then analyzed to determine the sulphur percentage. The used solvents are selective for the relatively polar oxidized sulphur containing compounds.

It is evident that this desulphurization process includes two stages: (i), oxidation in a first step; and (ii), liquid extraction at the end. The greatest advantages of the oxidative desulphurization process are low reaction temperature and pressure.

3- The effect of solvent extraction in diesel quality

The results of solvent extraction revealed some useful information about the extraction process. First, a solvent extraction has direct effect on the quality of diesel fuel, that is, some aromatic hydrocarbons are removed along with sulphones during the solvent extraction. This effect was evident in decreasing flash point of the desulphurized diesel fuel when it extracted by the solvent for more than one time. This in accordance with the literature [5]

Second, it was found that sum of solvent stayed in the diesel layer after one hour of extraction, but if the extraction left for overnight sum of diesel fuel was found in the solvent portion. The variation in diesel fuel volume was observed by measuring the fuel volume before and after extraction. This probably has to do with the solubility and phase separation of different hydrocarbons in diesel, which may depend on the volume ratio of solvent to solute. The smaller the ratio of solvent to the diesel the more difficult and longer time is required to have a good separation. However, a greater volume of solvent means a higher cost in term of the extraction and recovery process. In addition, the diesel lost increases with increasing volume of solvent. The effect of solvent extraction showed the same result at overnight, however the different time required have an efficient separation depends on the amount used.

The oxidation of organic sulphur compounds resulted in formation of sulphoxides and sulphones products that are relatively polar comparing to the original sulphur species. This gives preferences to sulphur compounds to be easily separated with minimum impact on removing other aromatic hydrocarbons. [5]

Results and discussion

1- Extraction of sulphur compound in diesel fuel by dimethylformamide (DMF), methyl alcohol, ethyl alcohol, diethyl ether, acetyl chloride, acetonitrile and other organic solvents without oxidation process were investigated. The investigation showed the removal of some sulphur organic compound. This is probably due to the small polarity differences between the sulphur organic compounds in diesel fuel.

After extraction, addition of tap water to DMF or acetonitrile yield in a milky white colloidal solution which disappeared in acetone or ethanol. Formation of this colloidal solution may due to large quantity of aromatics extracted simultaneously with the sulphones.Addition of tap water decrease the solubility of extracted aromatic and sulphone compounds in DMF or acetonitrile solvents.

The experimental results showed that the best solvent for sulphur organic compounds extraction was DMF [12]. This is due to higher polarity of DMF (Dielectric constant = 38, density = 0.944 g. cm^{-3}) than acetonitrile (Dielectric constant = 37.5, density = 0.786 g.cm^{-3}), (See fig.1), however mere polarity considerations are insufficient to define successful extraction solvents. Other properties to be considered include density, boiling point, freezing point, and surface tension.

2- The data of desulphurization of diesel fuel with different ratio of hydrogen peroxide to formic acid (v/v) at 25 to 50 ^{0}C shown in table 1.The temperatures above 80^{0}C are not recommended as it may lead to oxidation of other useful compounds present in fuels.[5]

The range of sulphur percent in the diesel sample before oxidation was1100 -1200 (ppm) Increasing the hydrogen peroxide ratio from 1 to 4 would result in a gradual increase in desulphurization efficiency and proportional to the peroxide concentration.

Table (1) Data of remaining sulphur percent (ppm) in desulphurized diesel fuel after extracting by DMF or acetonitrile

Ratio of hydrogen peroxide to formic acid (v/v)	remaining sulphur percent (ppm) - DMF	remaining sulphur percent (ppm) - Acetonitrile
1	520	750
2	410	680
3	320	520
3.5	310	330
4	190	480

Plots in figure (1) demonstrate the effect of hydrogen peroxide ratio to formic acid (v/v) versus remaining sulphur percent in desulphurized diesel fuel, and compare the efficiency of extraction by DMF to acetonitrile. It shows that the extraction with DMF is more efficient than extraction with acetonitrile

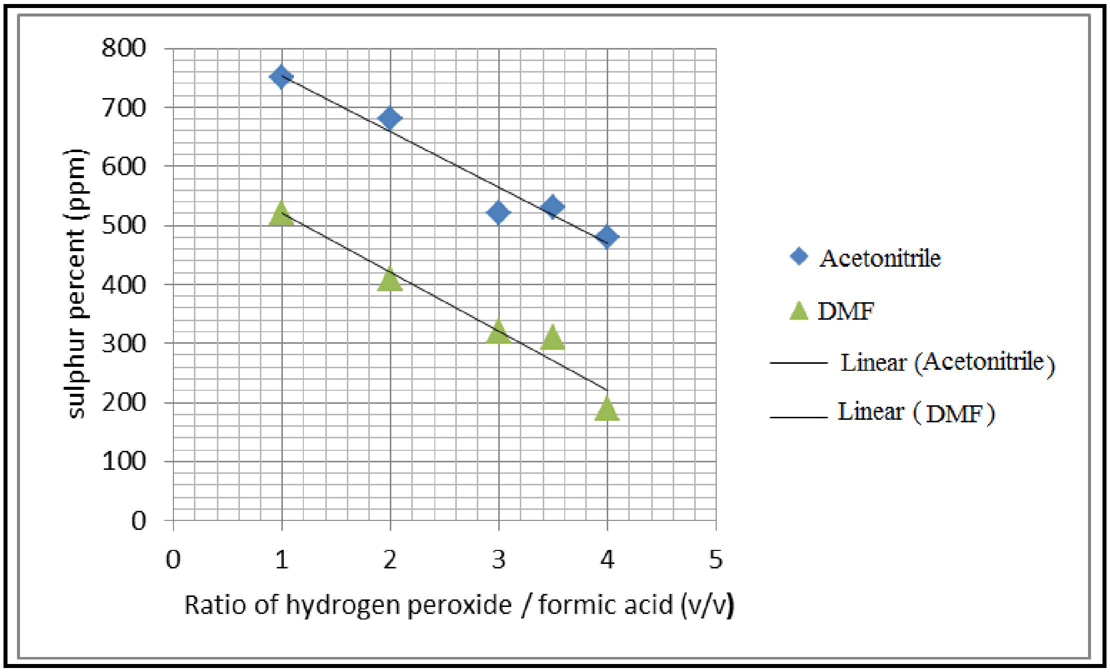


Fig. (1) Demonstrates that extraction of desulphurized diesel with DMF is more efficient than extraction with acetonitrile, and the effects of hydrogen peroxide concentration on removing organic sulphur compound from diesel fuel.

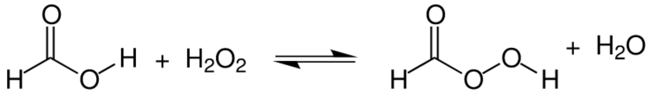
The efficiency of catalytically oxidative desulphurization depend on various factors, including concentration of organic sulphur compounds, concentration of oxidant, concentration of catalysts and exposure to radiation.

The untreated diesel fuel contains a large variety of organic sulphur compounds (thiols, sulphides, disulphides and thiophenes). [1] The reactivity of sulphur compounds for oxidation is increased with the increase of electron density on sulphur atom.[3] Several processes have been proposed in the past to deal with the problem of removing these compounds from diesel fuel. However, with the aid of catalysts and U.V. radiation, hydrogen peroxide can oxidize organic sulphur compounds to the corresponding sulphones in ambient conditions. Oxidative desulphurization (ODS) has been considered “green”, low cost and more efficient in oxidizing different kind of organic sulphur compounds in diesel fuel. After the desulphurization reaction, H_2O_2 decompose to H_2O and O_2, so there is no secondary pollution.

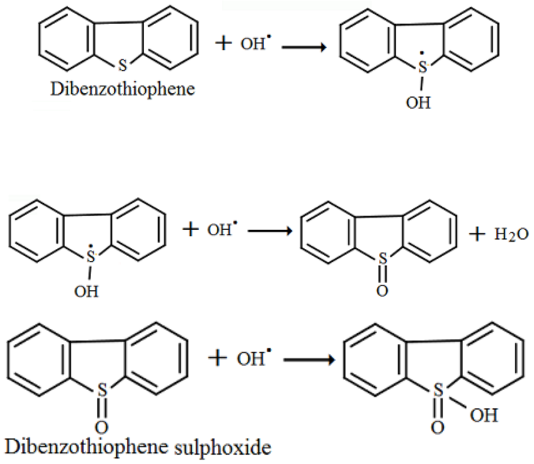
The role of the hydrogen peroxide and formic acid in oxidation process was suggested.
First H_2O_2 reacts with formic acid (HCOOH) quickly and generates very powerful oxidizing agent, peroxide acid (performic acid HCOOOH), and then the peroxide acid oxidize nonpolar sulphur compounds and form relative sulphones. [13,14,15,16,17]

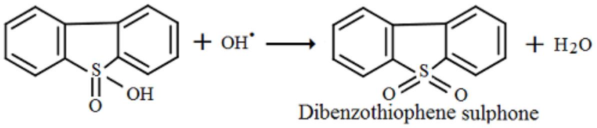
$$HCOOH + H_2O_2 \rightarrow HCOOOH + H_2O$$

The mechanism for the oxidation of dibenzothiophene to dibenzothiophenesulphones has been studied. The oxidation of dibenzothiophene (DBT) utilizes hydroxyl radicals produced by the photochemical decomposition of performic acid (HCOOOH). This decomposition is similar to that studied by Hunt and Taube [18]. The mechanism is summarized by the following equations:



Formic acid Performic acid





The data of variation of time of maximum temperature reached throughout reaction period (min.) versus the ratio of hydrogen peroxide / formic acid (v/v) in shown in Table (2).

Table (2) Data of variation of time of maximum temperature reached throughout reaction period (min) versus the ratio of hydrogen peroxide /formic acid (v/v)

Hydrogen peroxide /Formic acid (v/v)	Time of max. temperature (min.) reached
1	50
2	48
3	80
3.5	100
4	110

A plot (2) shows the ratio of hydrogen peroxide / formic acid (v/v), versus variation of time of maximum temperature reached throughout reaction period Figure (2).

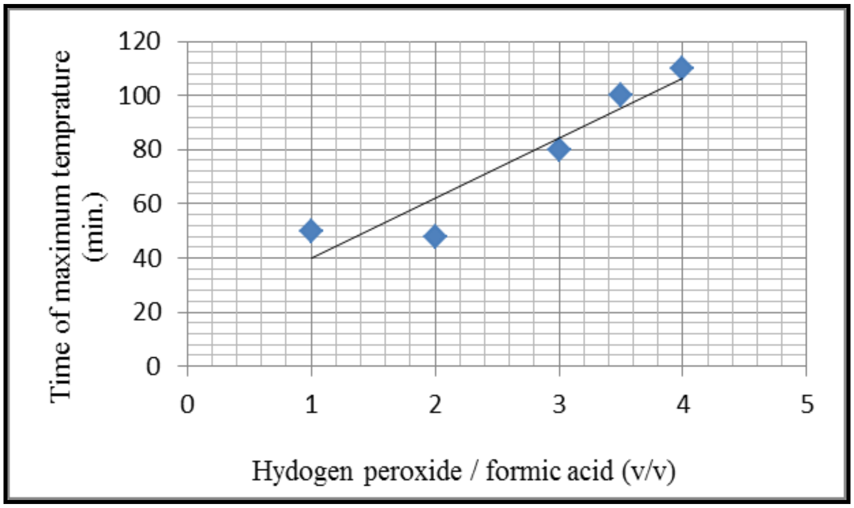


Fig. (2) Plot shows ratio of hydrogen peroxide / formic acid (v/v) versus variation of time of maximum temperature reached throughout reaction period (min.)

Figure (2) demonstrates that the increase in the time of the reaction is proportional to the increase in the ratio of peroxide to the acid. One can deduced that the increase in acid (the catalyst) concentration hasten the rate of the reaction. This is in contrast with other findings in the literature [19].

Proper quantities of catalysts can accelerate reaction and increase oxidation efficiency.

The reaction was conducted in the presence of two liquid reaction phases: an oil phase with the sulphur compound and a polar phase that contains the oxidant agent (H_2O_2), which is not soluble in the oil phase. In consequence, the overall sulphur removal rate is limited by the mass transfer between phases with very active catalysts. For this reason, an increase in the mass transfer clearly improves the overall sulphur removal rate. Attempts have been made employing fast stirring in order to give a high specific contact surface area between reactants. The data of variation of time of maximum temperature reached throughout reaction period (min.) versus the ratio of hydrogen peroxide / diesel fuel (v/v) in shown in Table (3).

Table (3) Data of variation of time of maximum temperature reached throughout reaction period (min.) versus the ratio of hydrogen peroxide / diesel fuel (v/v)

Hydrogen peroxide /diesel fuel (v/v)	Time of max. temperature (min) reached	Hydrogen peroxide /Formic acid (v/v)
0.02	45	1
0.04	50	2
0.08	60	3
0.12	80	3.5
0.14	90	4

A plot (3) shows the variation of time of maximum temperature reached throughout reaction period (min.) versus hydrogen peroxide / diesel (v/v), figure (3).

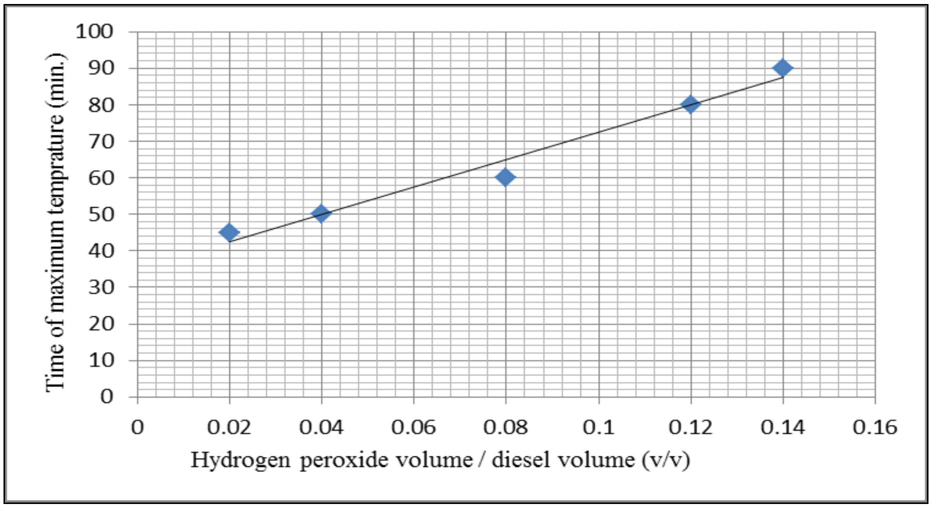


Fig. (3) A plot of variation of time of maximum temperature reached throughout reaction period (min) versus hydrogen peroxide / diesel (v/v)

Figure (3) demonstrates that the increase in the time of the reaction is proportion to the increase in the ratio of peroxide to the diesel. From experimental results obtained one can deduce that the cause of this increase in the time of reaction is due to effect of the ratio of hydrogen peroxide / formic acid in (v/v), see Table 2 and 3.

Photolysis of hydrogen peroxide in aqueous solution is another important aspect in aqueous photochemistry. UV irradiation with wavelength ranged from 200 nm to 280 nm, typically 254 nm, can be applied to dissociate hydrogen peroxide into hydroxyl radicals, hydrogen radicals and perhydroxyl radicals.[20] Instead of ground state hydroxyl radicals (•OH), excited state of hydroxyl radicals (•OH) can also be formed through a series of radical reactions.

In addition, organic sulfur compound is excited under light radiation as well, and then oxidized by excited state of hydroxyl radicals (•OH). However, most UV related desulfurization processes require use of high pressure mercury UV lamp with energy output greater than 200 watts, with irradiation time longer than 1 hour [21].

UV assisted oxidative desulfurization process could potentially be one of the next generations of desulfurization treatment technologies.

Challenges for oxidative desulphurization ODS

ODS has proved that it is possible to remove sulphur compounds from fuels to meet strict regulation limits. Among different chemical oxidants the best option is hydrogen peroxide. Using this oxidant, followed by extraction can reach very high levels of sulphur removal. However, in order to make an ODS process competitive with deep HDS a three-step process is needed: (i), improvement of the catalytic specific activity at low H_2O_2/S ratios and H_2O_2/Acid ratios; (ii), increase of the mass transfer in a biphasic system containing an oil fraction and polar phase; and (iii), enhancement of the post-treatment of sulfones produced.

Conclusions

The primary goal of this research is to develop better conditions, friend to environment and low cost procedure for reducing sulphur in diesel fuel and cut down the emission of SOx gases which is the main pollutant of the atmosphere and acid rain.

Recommendations for Future Work

✳ Greener chemicals, including oxidants, solvents and catalysts should be investigated in the future development.

✳ Conduct pilot-scale studies to optimize the process efficiency and assess its economic viability.

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