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A DESIGN FOR PHOTOCHEMICAL DESULFURIZATION AND SOLVENT EXTRACTION FOR LIGHT OIL

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The present invention relates to a method of a design suggested for a desulfurization of light oils through organic two phase liquid-liquid extraction, photochemical oxidation and photodecomposition of the sulfur compounds, using a high pressure mercury lamp. Photochemical desulfurization process is comprised of two stages. The first consist of the transfer of sulfur-containing compounds from the light oil to an aqueous-soluble polar solvent. This is then followed by the photooxidation and photodecomposition of the sulfur-containing compounds in the solvent by ultraviolet irradiation from a high pressure mercury lamp. The process is carried out under conditions of room temperature and atmospheric pressure. Solvent extraction with acetonitrile was investigated at differents oil/solvent ratios. After extraction with acetonitrile the sulfur content in gasoline decreased from 316 ppm to 47.7 ppm, and that in light gas oil from 988 ppm to 101.2 ppm or with 84.9 and 89.75 %, respectively. Mercury lamp photochemical process and effect of solvent have been discussed.

Keywords: photochemical, desulfurization, liquid-liquid extraction, light oil

Introduction

In the last ten years aroused considerable interest on the desulfurization of light oil and automotive fuels. Automotive fuels (gasoline, gas oil) create corrosive combustion by-products, releases sulfur oxides into the atmosphere, and increase deposits on fuel injection and combustion systems [1].

In automobile engines sulfur-containing compounds are converted to sulfur oxides (SO_x) after combustion and hence they are one of the main sources of acid rain and air pollution, which causes serious environmental problems in the world [4].

Sulfur-containing compounds are also undesirable in the refining processes because they tend to deactivate various catalysts used in downstream processing and in the upgrading of hydrocarbons. A catalytic hydrodesulfurization (HDS) method using Co-Mo, Ni-Mo or others catalysts were widely used in industirial scale, but required both high hydrogen pressure (up to 1, 000 psig) and high temperature (400 – 550°C), and to produce desulfurized fuels, the demand of hydrogen inevitably increased. In addition, the hydrodesulfurization method is complicated in the desulfurization of dibenzothiophenes (DBT) and its derivatives among sulfur-containing compounds in light oil [2, 3].

Mercury lamps as ultraviolet irradiation sources

There are three types of mercury arc discharge lamps, low pressure arc lamps (called also resonance lamps), medium pressure arc lamps, and high pressure arc lamps. A low pressure mercury lamp primarily emits two bands of irradiation, centered at 184.9 and 253.6 nm. These lamps operate at room temperature. Low pressure mercury lamps have a low total radiant flux (total radiant power) and for that reason they are often mounted parallel to or coiled about the reaction cell. The low pressure mercury lamps are applicable for the study of mercury-sensitized reactions and are often used where direct photolysis at 253.7 nm is desired in mercury-free systems. The absorption coefficients of mercury at 184.9 and 253.6 nm are so large that, the major fraction of the radiation of the lamp is absorbed by the mercury atoms, even if they are in a very low concentration. In order to avoid mercury-photosensitized reactions, all experimental devices should be free of mercury traces.

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Medium-pressure arc lamps operate at 1 atm or higher pressures, emit radiation of different wave lengths. At higher operating temperatures or pressures the lines tend to broaden, the longer-wavelength visible lines are increased in intensity, compared with those of shorter wavelengths and the continuum is increased to the line strength. The relatively high total radiant flux and the near-line character of the emission spectra make these lamps particularly well suited for photochemical use with monochromator and filter systems, and so they are extensively used in photochemical works [5].

High-pressure mercury lamps (commonly known as mercury arc capillary lamps) operate at very high pressure and are the most intensive source of ultraviolet, visible and infrared radiation. As these lamps operate at very high temperatures, forced-air, or circulating water cooling is required to avoid melting the quartz envelope. The minimum quantity of cooling water needed for a 300-500 W lamp is 1 to 3.5 litres/min.

High-pressure mercury lamps consist of a small-bore quartz tube with two electrodes immersed in mercury at either end. They operate on either alternating or direct current with suitable auxiliary ballast equipment. They have to be started in a horizontal position but operate in any position. Operation on direct current or vertically on alternating current leads to an unequal distribution of mercury. Each time before the lamp is switched on, it has to be taken out of the holder and checked for impurities and mercury distribution. At the same time, care must be taken to insure that the cooling water circulation is functioning properly and is deprived of air. The lamp must not switch on until the water is running [5].

Photochemical Processes

All photochemical processes obey four photochemical laws which can be applied generally in photochemistry:

- A photochemical reaction may occur only if light of sufficient energy is absorbed by the system.
- Each photon or quantum absorbed, activates only one molecule in the primary excitation step of a photochemical sequence.
- Each photon or quantum absorbed by a molecule has a certain probability of populating either the lowest exited singlet state (S_1) or the lowest triplet state (T_1)
- The lowest excited singlet (S_1) and triplet (T_1) states are the starting levels (in solution) of most organic photochemical processes.

Photochemical processes usually occur in two stages, the primary photochemical reaction is the reaction, which is directly due to the absorbed photon or quantum involving electronically excited states. This process was found to be independent on temperature. The secondary photochemical reactions (also called dark reactions) are reactions of radicals, radical ions and electrons which were produced by the primary photochemical reaction.

Most of the organic compounds, which emit luminescence (aromatic molecules) have an even number of π electrons, giving a ground singlet electronic state (S_0). *The Ground Singlet Electronic State* (S_0) is a state, in which the electron spins are paired. When a molecule absorbs electromagnetic radiation, its energy increases by an amount, equal to the energy of the absorbed photon. *Excited Singlet States* ($S_1, S_2, S_3, \ldots, S_i$) are formed after absorption of the photon. The spins of the π electrons are paired in singlet excited states. The photochemical reactions may occur mainly from the lowest excited singlet state (S_1) [6].

Effect of Solvent on Photochemical Reactions

The selection of a solvent is very important if photochemical reactions are studied in solution. There are probably very few photochemical reactions which are totally unaffected by the solvent. Too often the effect of the solvent is ignored when a photochemical reaction is under investigation. Any solvent used for the study of a photochemical reaction should satisfy the following requirements:

- The solvent should not absorb the incident light.
- Solvents should be spectrally or high-grade pure. Some impurities present in solvents may act as photosensitizers or quenchers.
- Solvents should be photochemically stable and should not participate in primary and secondary reactions. In many solvents, photooxidation reactions may occur much faster than the same reaction in pure reagents. Solvent radicals formed from photolysis of the solvent may react with reagents, completely changing the mechanism and kinetics of the observed reactions.

Knowledge of the photochemistry of solvents is necessary in order to correct the additional effects, which disturb the photoprocess.

Paraffinic Hydrocarbons and Alcohols are unreactive when irradiated in the 200-700 nm range but they may react if free formed in primary photochemical processes. *Benzene,* when irradiated with ultraviolet light in an oxygen-free atmosphere, can isomerize to fulvene and benzalvene, whereas in the presence of oxygen the ring-opening reaction produces long-chain conjugated dialdehydes. *Chloroform or Carbon Tetrachloride* during ultraviolet irradiation, produces very reactive $Cl^\cdot$ and. $CCl_3^\cdot$ free radicals. *Tetrahydrofuran(THF)* in the presence of oxygen, produces free THF radicals and final products of its reactions with oxygen, such as butyrolactone, α-hydroxytetrahydrofurane (HO-THF) and α-hydroperoxy-tetrahydrofurane (HOO-THF) [6].

Extractants were selected from among acetonitrile, propionitrile, butyronitrile, nitromethane, nitroethane, nitropropane, nitrobenzene, dimethylsulfoxide, N, N - dimethylacetamide, N-methylpyrrolidinone, trimethyl phosphate, triethylphosphate, hexamethylphosphoric amide, phosphorane [7].

Table 1 Properties of light oils used in extraction process

Property	Atmospheric Gasoline	FCC Gas oil
Density kg/m^3	0.7310	0.8702
Boiling point °C	78	220
Sulfur content wt %	0.0316	0.0988

Physical and Chemical Properties of Acetonitrile

Colourless liquid with structural formula (CH_3CN) and sweet ethereal odour. Transparent liquid with extraordinary fragrance like ether. Density (d_4^{15}) 0.7830 melting point -41 °C, boiling point 82 °C, flash point 5.56 °C. Soluble in water and alcohol, high dielectric constant, high polarity and strongly reactive.

Refractive index ($n\ _d^{20}$) 1.34423, viscosity 0.35 mPa/s at 20 °C. Critical temperature 274.7 °C, critical pressure 4.8332 mPa. Poisonous; flammable and when it burns the flame is bright.

Acetonitrile is poisonous and flammable. Its explosion range in the air is 3-16 %(vol %) [8, 9, 10].

Experimental Section

Materials

Atmosheric light gasoline and FCC light gas oil were supplied by Shanghai Refinery (*Table 1*). Acetonitrile of 99% purity was supplied by Shanghai Ling Feng Chemical Agents Company.

Analysis

After extraction, the gasoline and gas oil were tested for sulfur content. The sulfur content in both gasoline and gas oil was analyzed by standard test method for sulfur in petroleum products. (X-Ray Spectrometry, ASTM D 2622).

Results and Discussion

Apparatus and Procedure

The light gasoline and FCC gas oil were put in a flask and mixed vigorously with acetonitrile, using a magnetic stirrer. The oil, after 40 minutes of contacting with acetonitrile, was transferred with a polar solvent to a separatory funnel, shaked for 5 minutes and then the funnel was put on a carrier vertically for about 10-15 minutes until the two phases appeared clearly and the oil separated from the solvent. The extraction was investigated at 1, 2 and three stages and different volume ratios (1/1, 1/1.5, 1/2, 1/2.5, and 1/3)

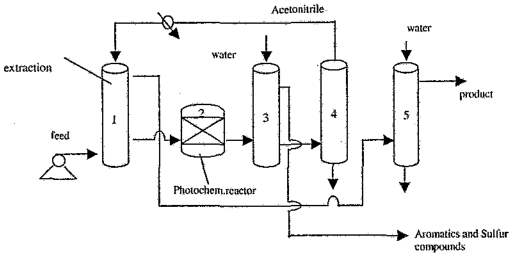

Fig.1 Flow diagram of photochemical reaction and desulfurization of light oil. 1. Extraction column; 2. photochemical reactor; 3. Acetonitrile elution column; 4. Acetonitrile distillation column; 5. Product washing column

Flow scheme

A flow scheme for photochemical desulfurization was constructed. The suggested scheme of this desulfurization process which includes the liquid-liquid extraction, photochemical oxidation and photodecomposition of sulfur-containing compounds, is shown on *Fig.1.* Light oil (gasoline or gas oil) and acetonitrile in the extraction column undergo liquid-liquid extraction. The product from the bottom of the column contains sulfur-compounds and acetonitrile. The extractor. The product, coming from the top of the column is desulfurized gasoline or gas oil. Acetonitrile is transferred to column No 2 (photochemical reactor) where the sulfur compounds are photodecomposed. in the presence of some external photoirradiation and oxidation. The reacted liquid is transferred to the acetonitrile elution column No.3, and water is added to remove the aromatics and sulfur compounds from the solvent. In the column acetonitrile and water mix, sulfur containing materials form product. At the same time acetonitrile-water mixture is transferred to No.4 washing /distillation column, while aromatics and sulfur compounds are leaving from the top of the column. After distillation, acetonitrile is recycled to the extraction column. The water phase from the bottom of the distillation column can be transferred to No.3 and 5 columns for recycling purposes. Since the desulfurization is finished in the column No.1 the desulfurized oil leaving the column No.1 contains minor quantities of acetonitrile, therefore in column No.5 water is used to remove the acetonitrile and purified product leaves the top of the column. This novel technology of extraction/ photooxidation and photodecomposition process is used for the first time in this country for removing sulfur compounds from light oils (gasoline, gas oil, etc.). The desulfurization method should be a distinct line in technological methods, The efficiency can be improved by adding oxidation agent. Besides, this method has high desulfurization efficiency (89 % and above), low investment cost, operation conditions (temperature, pressure) are moderate and extractant can be recycled. There are various applications for generated sulfur-containing compounds. These materials can be utilized in atomic industry, as a special feature. This has a bright scope from the high quality research and valuable point of view.

Table 2 Sulfur Contents of Gasoline After Extraction With Acetonitrile

Sample No.	Extraction Stage	Oil/Solvent Volume ratio	Sulfur Content ppm
1	1 Stage	1/1	158.5
2	1 Stage	1/1.5	133.8
3	1 Stage	1/2	109
4	1 Stage	1/2.5	96.2
5	1 Stage	1/3	85.4
6	2 Stages	1/1	117.3
7	2 Stages	1/1.5	80.7
8	2 Stages	1/2	55.9
9	2 Stages	1/2.5	55.2
10	2 Stages	1/3	49.7
11	3 Stages	1/1	110.2
12	3 Stages	1/1.5	72.9
13	3 Stages	1/2	54.9
14	3 Stages	1/2.5	51.3
15	3 Stages	1/3	47.7

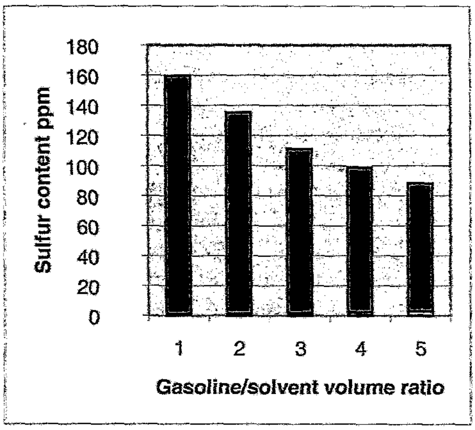

Fig.2 Sulfur content in gasoline after 1 stage extraction with acetonitrile at different oil/solvent volume ratios

Liquid-Liquid Extraction

The extraction of the sulfur-containing compounds from two light oils (atmospheric gasoline and FCC gas oil) were investigated by contacting both of the two oils with acetonitrile at room temperature and atmospheric pressure. Acetonitrile was contacted with the oil for 40 minutes and transferred to a seperation funnel and after ten minutes, the oil phase was separated from the acetonitrile phase. After extraction, the light oil appeared more clean and pure. The extraction of atmospheric gasoline and FCC gas oil were investigated at different volume ratios of oil/solvent (1/1, 1/1.5, 1/2, 1/2.5, 1/3). The rate of the desulfurization was found to increase effectively with increasing the extraction stage. In the same time the desulfurization rate was increased with increasing the ratio of the solvent in the total (oil/solvent) solution volume. This is shown on the *Tables 2 and 3* and on the *Figs.2 to 7*. The yield of desulfurized oil is varying according to the oil/solvent volume ratio and the extraction stages (1, 2, and 3 stage). The yield of raffinate varies from 78 to 52 vol% for light gasoline, and from 68 to 43 vol% for light gas oil. The sulfur content for gasoline was decreased from 318 ppm to 47.7 ppm, and that for gas oil from 988 ppm to 101.2 ppm after extraction or with 84.9 % for gasoline and 89.75 % for gas oil.

Table 3 Sulfur Contents of Gas Oil after Extraction with Acetonitrile

Sample No.	Extraction Stage	Oil/Solvent Volume ratio	Sulfur Content ppm
1	1 Stage	1/1	594
2	1 Stage	1/1.5	465
3	1 Stage	1/2	453
4	1 Stage	1/2.5	389.5
5	1 Stage	1/3	227.6
6	2 Stages	1/1	431
7	2 Stages	1/1.5	259.7
8	2 Stages	1/2	214.7
9	2 Stages	1/2.5	158.4
10	2 Stages	1/3	113.3
11	3 Stages	1/1	398.4
12	3 Stages	1/1.5	267.5
13	3 Stages	1/2	200.6
14	3 Stages	1/2.5	114.1
15	3 Stages	1/3	101.2

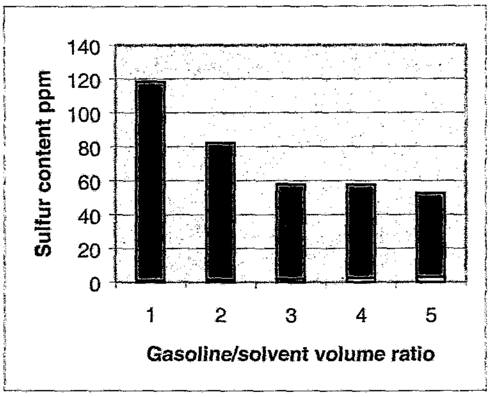

Fig.3 Sulfur content in gasoline after 2 stage extraction with acetonitrile at different oil/solvent volume ratios

Conclusions

A liquid-liquid solvent extraction of sulfur compounds in light oil (atmospheric gasoline and and FCC gas oil was investigated with the following results:

- After the extraction with acetonitrile, the sulfur compounds being in gasoline were decreased from 318 ppm to 47.7 ppm and that in gas oil from 989 ppm to 101.2 ppm.

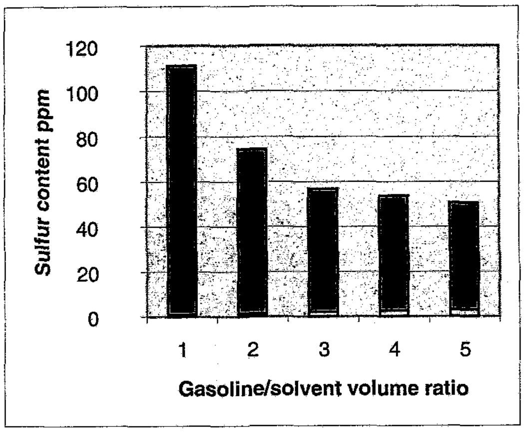

Fig.4 Sulfur content in gasoline after 3 stages extraction with acetonitrile at differents oil/solvent volume ratios

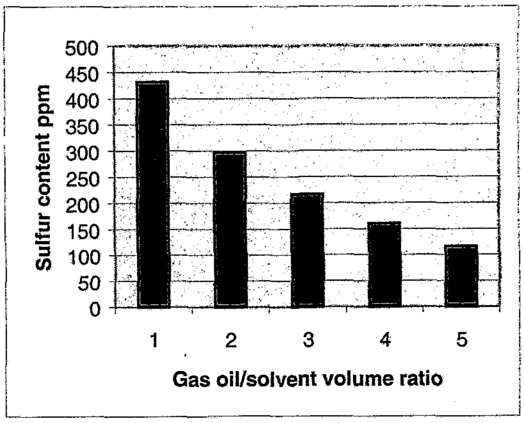

Fig.6 Sulfur content in gas oil after 2 stages extraction with acetonitrile at differents oil/solvent volume ratios

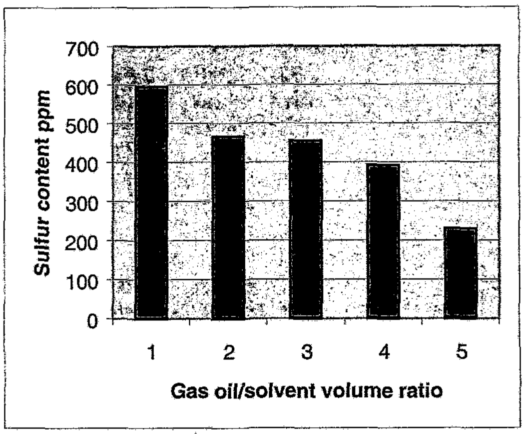

Fig.5 Sulfur content in gas oil after 1 stage extraction with acetonitrile at differents oil/solvent volume ratios

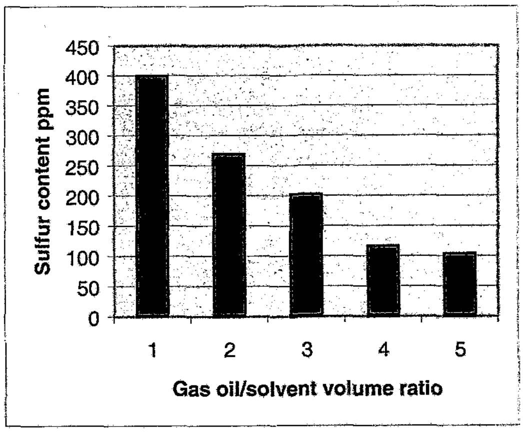

Fig.7 Sulfur content in gas oil after 3 stages extraction with acetonitrile at differents oil/solvent volume ratios

- The transfer of sulfur-containing compounds from the light oil to the solvent was found to proceed more effectively in gas oil *(89.6%) than* that in gasoline (85%)
- A flow diagram for desulfurization was investigated.
- The generated sulfur will be used in atomic industry production.

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