Desulphurization of Crude Oil by Ultrasound Integrated Oxidative Technology

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Abstract— The crude oil which contain high amount of sulphur proves to be deteriorative for our environment, hence desulfurization of crude oil is imperative. Since the 17th century industrialization the use of crude oil has grown exponentially and hence the amount of oxides of sulphur in the atmosphere, which can proves to be catastrophic as far as the health of our planet is concerned. Therefore, in this study a method for the removal of sulphur from sour crude oil using ultrasound-assisted oxidative process has been proposed. This method is actually a combination of oxidation and applying ultrasonic waves to achieve very low sulphur content of crude oil.

Key words: Crude Oil, Desulfurization, Ultrasound-Assisted Oxidative Process

I. Introduction

We know crude oil is a sulphur-containing organic and inorganic compound. The amount of sulphur is one of the most important factors of crude oil's price. Sulphur containing compounds in crude oil, petroleum, diesel and other fuel oils include sulphides, thiols, thiophenes, substituted benzo- and dibenzothiophenes (BTs and DBTs), benzonapthothiophene (BNT), and many more complex molecules, in which the condensed thiophenes are the most common forms. Hielscher ultrasonic reactors assist the oxidative deep desulfurization process required to meet the today's stringent environmental regulations and ultra-low sulphur diesel (ULSD, 10ppm sulfur) specifications.

Types of impurities present in crude oil:

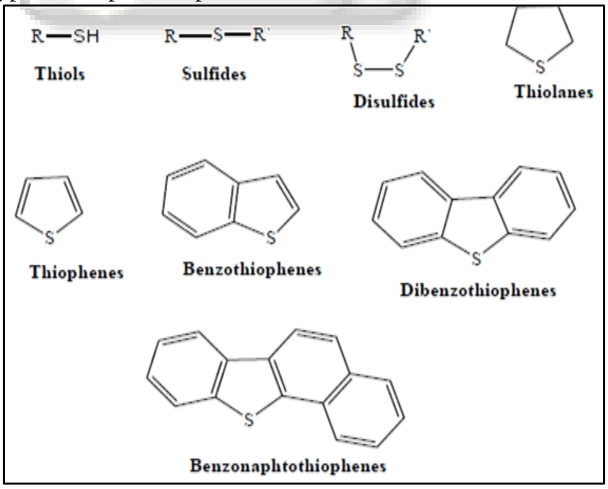

Fig. 1:

Sulphur compounds in the refining process are undesirable because it can lead to deactivation of the catalyst and also causes environmental pollution.

In order to control air pollution because of heavy petroleum fractions combustion, most of the countries released a new regulation requiring the use of low-sulphur petroleum fractions. It means that the sulphur content of petroleum fractions used in vehicles be limited to 50 ppm.

It is possible, however, to operate at too high temperature for maximum sulphur removal. Hydrotreating requires high temperature and pressure up to 340ºC and 31kg/cm^2 pressure.

Ultrasound-assisted oxidative desulfurization (UAOD) has been developed as an alternative technology to the traditional hydrotreating, which suffers from significant costs associated with high-pressure, high-temperature hydrodesulphurization equipment, boilers, hydrogen plants, and sulphur recovery units. Ultrasound-assisted oxidative desulfurization permits carrying out the process under much milder conditions, faster, safer and much more economically.

During the past years, alternative technologies have been studied, among which ultrasound-assisted oxidative desulfurization has found a wide attention. Ultrasound-assisted oxidative desulfurization method for sulphur omission has main benefit compared to other common methods like HDS. Oxidative desulfurization technology as a promising method for deep removal of sulphur under mild conditions has been discussed. This method in comparison to HDS requires much less pressure, temperature and operating costs. This method is based on the oxidation of sulphur compounds and finally the formation of sulphoxides or sulfones. These materials are highly polar and therefore more easily by extraction with solvent or adsorption can remove them from the oil.

A. *Oxidative Desulfurization (ODS)*

Oxidative Desulfurization (ODS) Oxidative desulfurization with hydrogen peroxide and subsequent solvent extraction is a two- stage deep desulfurization technology to reduce the amount of organosulfur compounds in fuel oils. Hielscher ultrasonic reactors are used at both stages to improve phase-transfer reaction kinetics and dissolving rates in liquid-liquid phase systems.

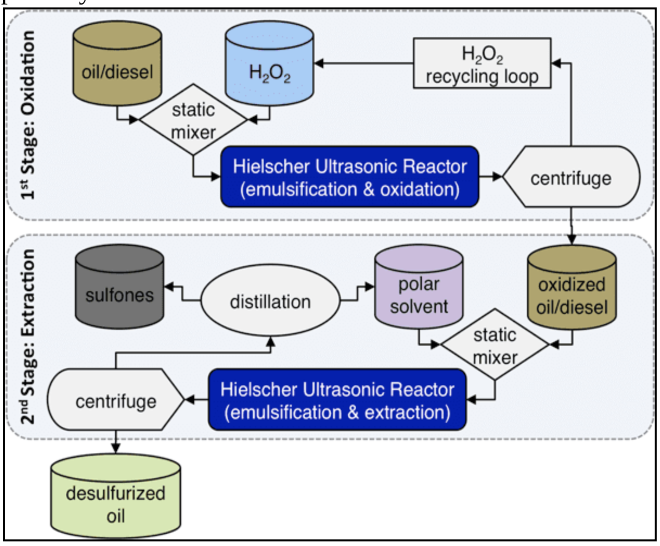

Fig. 2: Flowchart for Ultrasonically Assisted Oxidative Desulfurization – 2 Stages

B. Ultrasound-Assisted Oxidative Desulfurization

Ultrasound-assisted oxidative desulfurization is a very attractive alternative to the traditional hydro desulphurization technology. Exposing liquids to high-intensity ultrasound greatly promotes mass transfer-limited reactions and surface chemistry of catalysts. Ultrasound creates acoustic cavitations, which produces violently imploding vacuum bubbles, causing shock waves, micro-jets and strong shear forces as well as extreme local temperatures (~5,000 K) and pressures (~1,000 atm). These extreme conditions result in exceptionally efficient mixing, yielding nanoemulsions with very small droplet sizes and enormous contact areas between all components. The oxidative desulfurization of crude oil is, therefore, considerably accelerated by exposure to high-intensity ultrasound.

At the first stage of ultrasonically assisted oxidative desulfurization, hydrogen peroxide is used as an oxidant to selectively oxidize the sulphur-containing molecules that are present in fuels oils to their corresponding sulfoxides or sulfones under mild conditions to increase their solubility in polar solvents with an increase in their polarity. At this stage, the insolubility of the polar aqueous phase and the nonpolar organic phase is a significant problem in the process of oxidative desulfurization as both phases react with each other only at the interphase. Without ultrasonics, this results in a low reaction rate and a slow conversion of organosulfur in this two-phase system.

II. METHODOLOGY

In oxidation process, sulphides are oxidized to sulfones or sulphoxides by using proxy acids such as hydrogen peroxide and acid-carboxylic. A useful method for desulfurization of oil using organic acids and hydrogen peroxide according to the following reaction is suggested.

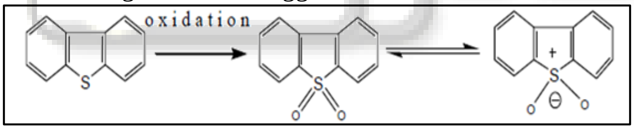

Fig. 3:

Despite the good performance of this kind of desulfurization (oxidation using organic acids), this method is very time consuming and it may be necessary to compensate for the use of metal catalysts. Therefore, to minimize reaction time, ultrasonic irradiation can provide the optimum conditions for chemical reactions without catalysts.

The oxidative desulfurization of crude oil is commonly done by mixing it with an oxidant, a catalyst and a phase-transfer agent (e.g. hydrogen peroxide solution in water, formic and/or acetic acid, quaternary ammonium). During the process, sulphur-containing compounds in crude oil are converted to polar sulphur oxides and sulfones, which are subsequently removed via selective adsorption or extraction. However, since all added reagents are water-based, they do not readily mix with the crude oil and must be emulsified. The reaction is mass transfer-limited and its rate strongly depends on the mixing efficiency and the resulting size of the contact surface area between the water and the oil phases.

A. The Importance of High Ultrasonic Amplitudes

Ultrasonic intensification of commercial-scale oxidative desulfurization of crude oil requires the use of an industrial-size flow-through ultrasonic processor able to maintain high vibration amplitudes of about 80 - 100 microns. The amplitudes directly relate to the intensity of ultrasonic cavitations-generated shear forces and must be maintained at a sufficiently high level for the mixing to be efficient. Similar amplitudes are required for the production of high-quality – a process which is a prerequisite for mass transfer-limited reactions.

Ultrasound-assisted oxidative desulfurization (UAOD) process was applied to diesel oil and petroleum product feedstock containing model sulphur compounds (benzothiophene, dibenzothiophene and dimethyldibenzothiophene). The influence of oxidant amount, volume of solvent for the extraction step, time and temperature of ultrasound treatment (20 kHz, 750 W, operating at 40%) was investigated. Using the optimized conditions for UAOD, sulphur removal up to 99% was achieved for model compounds in petroleum product feedstock using a molar proportion for H_2O_2:acetic acid:sulfur of 64:300:1, after 9 min of ultrasound treatment at 90°C, followed by extraction with methanol (optimized solvent and oil ratio of 0.36). Using the same reagent amount and 9 min of ultrasound the removal of sulphur was higher than 75% for diesel oil samples. Sulphur removal without ultrasound using the same conditions was lower than 82% for model compounds and 55% for diesel oil samples showing that ultrasound improved the efficiency of oxidative desulfurization. In comparison to conventional hydrodesulphurization, the proposed UAOD process can be performed under relatively mild conditions (atmospheric pressure and 90°C, without using metallic catalysts).

III. RESULTS

Experiments show that ultrasonic irradiation enhanced desulfurization reaction. Desulfurization efficiency was about 93.2% when ultrasound was used. However, when ultrasonic irradiation wasn't used (reaction with mechanical stirring) even after 20 min, desulfurization efficiency was less than 62.5%.

IV. CONCLUSION

Based on study, it can be suggested that oxidative desulfurization method using ultrasound is a useful, cheap and easy method for desulfurization of crude oil. It requires less temperature and pressure when compared to hydrotreating process.

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