



Removal of organosulfurs from liquefied petroleum gas in a fiber film contactor using a new formulated solvent



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ABSTRACT

H₂S and organosulfurs were simultaneously removed from delayed coking LPG in a fiber film contactor using several formulated solvents (named UDS-I, UDS-II, UDS-III, and UDS-IV). The mass transfer rate of organosulfurs in the proposed process was compared with that of conventional countercurrent columns using *N*-methyl-diethanolamine (MDEA) solvent in terms of three aspects. Additionally, the optimum solvent was observed and the influences of operation conditions on desulfurization performance were systemically investigated. The results indicate that the fiber film contactor has greater mass transfer area than conventional countercurrent columns. UDS-IV solvent possesses the highest total removal of organosulfurs, which is 45.7 percentage points higher than that of MDEA. Meanwhile, the distribution ratios of organosulfurs in UDS-IV/LPG system are found 7–10 times as high as those in MDEA/LPG system. The diffusion coefficients for organosulfurs in UDS-IV solution are found the highest, up to 1.08 times as high as those in MDEA solution. As a result, the process combining UDS-IV solvent and the fiber film contactor exhibits excellent performance for simultaneously removing H₂S and organosulfurs, owing to the increase in mass transfer area, driving force and mass transfer coefficient. Under optimum operation conditions, UDS-IV solvent can reduce the contents of H₂S and total sulfur in the LPG to less than 1 and 240 mg/Nm³, respectively, and the total removal of organosulfurs is above 93%.

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1. Introduction

Liquefied petroleum gas (LPG) usually contains various hazardous sulfur compounds, i.e., H₂S, COS, CS₂, mercaptans, thioethers, and disulfides [1]. Therein, methyl mercaptan dominates the total content of organosulfur in LPG. Prior to commercial application, the sulfur compounds in LPG should be effectively removed in order to meet certain specifications. A common LPG desulfurization technology contains mainly two processes: alkanolamine treating for H₂S removal and caustic treating for methyl mercaptan removal. Due to very limited organosulfurs removal performance of alkanolamine solvents used in present industrial plants [2,3], LPG scrubbed with alkanolamines needs to be further treated with caustic solution to remove residual mercaptans [4]. However, caustic treating consumes large amount of sodium hydroxide and discharges caustic sludge that causes severe environmental pollution [5].

The development of an efficient and environment-friendly desulfurization process for LPG is becoming an urgent problem and attracting increasing attention. As to the alkanolamine treating process, the total removal of organosulfurs can be improved from two aspects: improving the desulfurization performance of solvent and enhancing the mass

transfer efficiency in the liquid–liquid contactor. A series of formulated solvents based alkanolamine (labeled as UDS solvents) have been developed in this laboratory and used to efficiently remove H₂S and organosulfurs from natural gas [6,7]. The fiber film contactor possesses desirable characteristics of non-dispersion contacting and great surface area for mass transfer between two liquid phases [8,9], leading to higher mass transfer efficiency as compared with conventional columns. Therefore, it has been widely applied in caustic treatment for removing mercaptans from LPG and gasoline [10]. So far, it is rarely reported in literatures that the fiber film contactor is applied in alkanolamine treating units.

The desulfurization process with combining the optimum UDS solvent and the fiber film contactor was proposed here, aiming at minimizing the total sulfur content in LPG exported from alkanolamine treating units. The mass transfer rate of organosulfurs in the proposed process was compared with that in the conventional treating process employing countercurrent columns and *N*-methyl-diethanolamine (MDEA) in terms of mass transfer area, driving force and diffusion coefficient. In addition, the optimum solvent composition was observed and the effect of operation conditions on the desulfurization performance was discussed. The research results provide a promising process for simultaneously removing H₂S and organosulfurs from LPG. Such combined process can significantly reduce the desulfurization stress, sodium hydroxide consumption and caustic sludge emission, therefore, it is more economical and environment-friendly.

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2. Experimental section

2.1. Materials

The UDS solvents are formulated by adding a primary alkanolamine, a secondary alkanolamine, a five-membered sulfur-containing heterocyclic compound (denoted as 'SUL', a structural analog of sulfolane), a six-membered nitrogen-containing heterocyclic compound (denoted as 'CA', a structural analog of morpholine or piperazine) and a six-membered nitrogen containing unsaturated heterocyclic compound (denoted as 'CUA') to MDEA, which is the main composition [6,7,11,12]. These compounds are mixed with different proportions to prepare UDS-I, UDS-II, UDS-III and UDS-IV solvents, respectively. MDEA was provided by Jiangsu Jinlu Environmental Technology Co., Ltd. (China). The difference in properties of MDEA and UDS solvents are shown in Table 1. As exhibited in Table 2, the total organosulfur content in the delayed coking LPG is up to 3420.3 mg/Nm³, 79.2% and 19.6% of which are accounted for methyl mercaptan and COS, respectively.

2.2. Experimental apparatus and procedure

As illustrated in Figs. 1 and 2, the fiber film contactor is consisted of a liquid distributor, a mass transfer zone, and a separation vessel. The mass transfer zone is a vertical stainless steel vessel with height of 1050 mm and inner diameter of 57 mm, respectively. The hydrophilic metallic fibers with diameter of 0.11 mm are placed in the mass transfer zone as the filling.

The desulfurization aqueous solution (aqueous phase) is firstly pumped to the mass transfer zone via the liquid distributor located on the top of the fiber film contactor, then flows down along the fibers and forms thin films. Liquid LPG (hydrocarbon phase) is then introduced into the mass transfer zone and contacts with descending aqueous phase over the aqueous film, and such a liquid–liquid contact allows a high efficiency for mass transfer. Thereafter the two-phase mixture is collected in the separation vessel, and is separated immediately into two layers because of their different densities.

2.3. Analytical method

The sulfur compounds in LPG were determined using a gas chromatograph coupled with a flame photometric detector [6]. The total organosulfur content in aqueous solution was determined using a micro-coulometric analyzer. Prior to micro-coulometric analysis, each aqueous solution sample was pretreated to eliminate the interference of H₂S [13].

2.4. Removal of organosulfur

The removal of organosulfur (E) is calculated from the following equation:

$$E = 1 - \frac{c_2}{c_1} \frac{1 - \varphi(\text{H}_2\text{S})_1}{1 - \varphi(\text{H}_2\text{S})_2} \quad (1)$$

Table 1
Properties of UDS solvents and MDEA.^a

Solvent	Density (kg/m ³)	Viscosity (mm ² /s)	Surface tension (mN/m)	Proportion ^b
UDS-I	1028.5	31.14	20.8	10:90
UDS-II	1029.8	27.33	20.6	20:80
UDS-III	1031.2	24.57	20.4	30:70
UDS-IV	1033.0	23.96	20.4	40:60
MDEA	1027.2	33.60	20.6	

^a Properties determined at 40 °C.

^b Mass ratios of formulated components (rest components except MDEA) to MDEA in UDS solvents.

Table 2
Distribution of SCCs in delayed coking LPG.

SSC	Content (S) (mg/Nm ³)
H ₂ S	28600
COS	670.6
Methyl mercaptan	2710.4
CS ₂	5.6
Ethyl mercaptan	15.1
<i>i</i> -propyl mercaptan	2.4
<i>n</i> -propyl mercaptan	2.0
Dimethyl disulfide	14.1
Total organosulfur	3420.3

where c_1 and c_2 are the contents of organosulfur in gas LPG before and after desulfurization, respectively, mg/Nm³; $\varphi(\text{H}_2\text{S})_1$ and $\varphi(\text{H}_2\text{S})_2$ are the volume fractions of H₂S in gas LPG before and after desulfurization, respectively.

2.5. Distribution ratio of organosulfurs

The distribution ratio of organosulfurs (α), which is defined as the total organosulfur content ratio of rich solution to treated LPG, is expressed as follows:

$$\alpha = \frac{c_a/\rho_a}{c_h/\rho_h} \quad (2)$$

where c_a is the total organosulfur content in rich solution, mg/L; c_h is the total organosulfur content in treated LPG, mg/Nm³; ρ_a is the density of rich solution, kg/L; and ρ_h is the density of treated LPG, kg/Nm³.

3. Results and discussion

3.1. Mass transfer rate of organosulfurs between two phases

Organosulfurs transfer from the hydrocarbon phase into the aqueous phase in the LPG desulfurization process, thus the mass transfer rate of organosulfurs governs the removal efficiency. The mass transfer rate [10] can be calculated from the following equation:

$$N_{os} = K \cdot A \cdot \Delta C \quad (3)$$

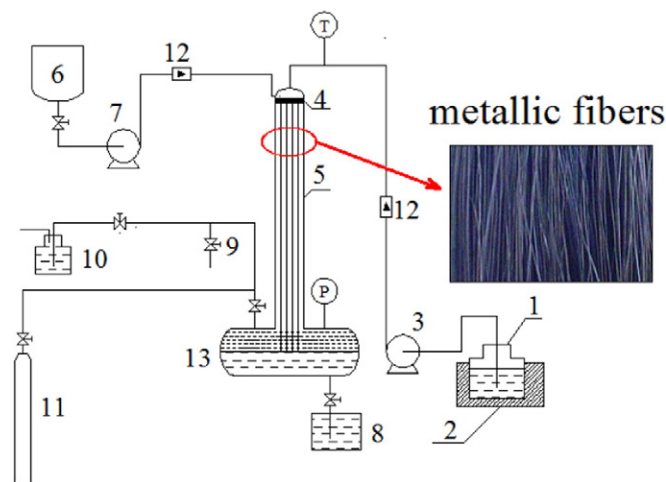


Fig. 1. Schematic diagram for LPG desulfurization process equipped with a fiber film contactor. 1—desulfurization solution tank; 2—thermostatic water bath; 3—solution pump; 4—liquid distributor; 5—mass transfer zone; 6—LPG tank; 7—LPG pump; 8—rich solution tank; 9—sampling port; 10—tail gas absorber; 11—nitrogen cylinder; 12—flowmeter; and 13—separation vessel.

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