

Investigation of Mercaptan Removal from Kerosene Using Passive Mixing Tools: Experimental Study and CFD Modeling

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ABSTRACT

In this work, the role of appropriate mixing for mercaptan removal from Kerosene using caustic soda has been investigated in the pilot scale. Static mixer in different conditions has been used as a passive mixing tool to achieve proper mixing, thus high performance of mercaptan removal. Two lengths of static mixer, including 20 and 40 cm, as well as two pitches 1 and 3 mm were considered in a straight line. NaOH was injected to the Kerosene line to remove (convert it to disulfide) the mercaptan. The effects of mixer length and mixer element pitch at different flow rates of Kerosene, including 2, 18 and 30 mL/s were investigated on the mercaptan removal. The experimental results showed that the concentration of mercaptan in the pilot line outlet will decrease as the flow rates of Kerosene decrease. Also, at a fixed flow rate of Kerosene, increasing the length of the static mixer and decreasing its element pitch caused the mercaptan to decrease due to proper mixing. Computational Fluid Dynamics (CFD) modeling technique was employed to describe the experimental results, fluid flow pattern, and mixing performance. Qualitative predicted results of CFD modeling show good agreement with the experimental data.

1. Introduction

Mercaptans are a kind of organic sulfides widely prevalent in petroleum products such as Gasoline, Kerosene, jet fuel, Diesel and heating oils [1]. They can cause serious corrosion problems, and most of them are highly toxic with invasive odour [2]. Therefore, it is necessary to remove them by the methods known for mercaptan removal such as reaction, absorption, adsorption and oxidation [3].

Mixing is one of the more practical

operations in the chemical processes involving manipulation of a heterogeneous physical system to achieve homogeneous compound. Modern industrial processing almost always involves some form of mixing. Using the correct equipment, it is possible to mix a solid, liquid, or gas into another solid, liquid, or gas [4].

Different types of mixers in industry include dynamic mixers, where mixing is accomplished by the rotating action of an impeller in the continuous fluid and static

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mixers, as the streams move through the mixer and the non-moving elements continuously blend the materials. Static mixers are now commonly used in the chemical and petrochemical industries to perform continuous operations.

The effectiveness of static mixers to mix miscible fluids or to enhance heat transfer is due to the continuous splitting, extension and transportation of the components. Each element of a static mixer is a specially designed rigid structure that divides the flow and recombines it in a geometric sequence so that diffusion or conduction becomes rapid [5-7].

Numerous studies were performed on mixing using passive mixing tools. Hobbs [8] improved the mixing performance of the Kenics mixer. Three geometric parameters were investigated: the twist direction of adjacent elements, the element length-to-diameter ratio, and the amount of twist per element.

Micromixing in a static mixer and an empty tube to determine the influence of motionless mixing elements on the micromixing time were studied by Meyer et al. [9]. They found that the mixing time is about 10 times larger in an empty tube than in the static mixer.

Fang and Lee [10] published a study on the micro-mixing efficiency of static mixers using fast competing reactions as a test system. They showed experimentally that Kenics mixers significantly improve micromixing, both in the laminar and turbulent flow regimes.

Eric Fourcadea et al. used CFD technique and developed a new method to calculate the average value of the rate of striation thinning from the flow field in a static mixer. They showed that a micromixing theory could be adequately coupled to the accurate description

by this method [11].

Christian Lindenberg et al. investigated the mixing in static mixers experimentally and numerically. It was shown that not only experimental results and model predictions are in good agreement for all mixer geometries and operating conditions, but also CFD serves as a valuable tool to improve or to scale up mixer [12].

The present study aims to solve an industrial problem using a pilot scale study. Construction of mercaptan removal unit for some refineries is not practical and economical. At this condition, mercaptan removal is done by injection of a mercaptan scavenger. Due to no effective mixing in the pipeline, the mercaptan concentration in the fuel storage tank is not in an acceptable range, so using static mixers in the pipeline can improve the quality of mixing.

In the present work, removal of mercaptans from untreated Kerosene using caustic soda has been performed in the presence of static mixers. The aim of this study is to evaluate the effect of flow rate, mixer length and mixer element pitch on the mixing progress and mercaptan removal performance. Experiments were performed in the cases of no static mixer and two mixers lengths as well as two-element pitch at three flow rates of the Kerosene. Flow rates were chosen, such that the flow remains in the laminar regime. In addition, CFD modeling is used to visualize mixing and reaction zones in the mixer. Moreover, the effects of Operational parameter, such as flow rate, on velocity magnitude and mass transfer of mercaptan and disulfide were investigated.

2. Materials and apparatus

The materials used in this system contain untreated Kerosene (with initial concentration

of 135 ppm of mercaptan) and caustic soda to treat the Kerosene in the pilot line. In order to study this process, untreated Kerosene enters the pilot line and caustic (1 molar NaOH solution) is injected near the line inlet. As the Kerosene goes through the line, it mixes and reacts with the injected caustic soda to convert and remove the mercaptan.

Mercaptan is oxidized to disulfide by air under caustic condition. Air provides the oxygen, while caustic soda provides the alkalinity. Oxygen reacts with mercaptan through the following reaction [13]:



Removal of mercaptans by extraction starts

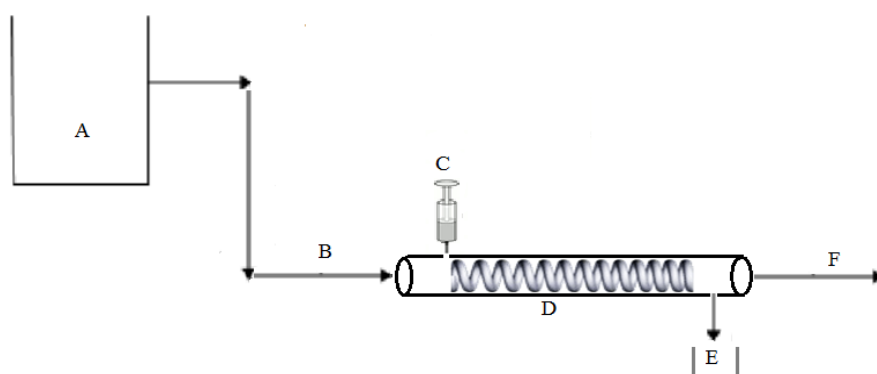


Figure 1. A schematic diagram of experimental setup (A=Kerosene tank, B=Kerosene stream, C=NaOH, D=Pipe and its static mixer, E=Sampling, F=Waste).

3. Modelling

In order to better understand mixing progress and mercaptan removal performance in the pilot-scale pipeline, mixing process in the line was modelled using CFD technique in steady-state condition. One phase of CFD modeling was carried out and species transport model was employed to study the diffusion and mixing of the caustic soda in the main Kerosene flow. The solution domain was divided into 1387609 unstructured tetrahedral meshes; the continuity, momentum and scalar transport equations were applied to all of the

with dissolving them in caustic soda based on the following reaction:



The pilot line is a tube of 80 cm in length and 1 cm in diameter. To improve the quality of mixing, a coil element of static mixer was located in the line. Two lengths of static mixer as 20 and 40 cm and two elements of pitches as 1 and 3 mm were used in the experiments. Figure 1 shows a schematic of the pilot experimental setup with its injection and sampling points. Samples were collected from the outlet stream and analyzed to determine the mercaptan value.

control volumes and solved simultaneously as follows [14]:

Continuity equation:

$$\frac{\partial u_i}{\partial x_i} = 0 \quad (1)$$

Momentum equation:

$$\rho u_i \frac{\partial u_i}{\partial x_i} = -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_i} \left[\mu \left(\frac{\partial u_i}{\partial x_i} + \frac{\partial u_j}{\partial x_j} \right) - \overline{u_i u_j} \right] \quad (2)$$

Scalar transport equation:

$$\frac{\partial \Phi}{\partial t} + \text{div}(\Phi U) = \text{div}(\Gamma_\Phi \text{grad} \Phi) + \left[-\frac{\partial \overline{u \Phi}}{\partial x} - \frac{\partial \overline{v \Phi}}{\partial y} - \frac{\partial \overline{w \Phi}}{\partial z} \right] + S_\Phi \quad (3)$$

Fig. 2 shows a part of the meshed pipeline equipped by the static mixer. Fine meshes

were used for the injection region to enhance the solution accuracy in this region.

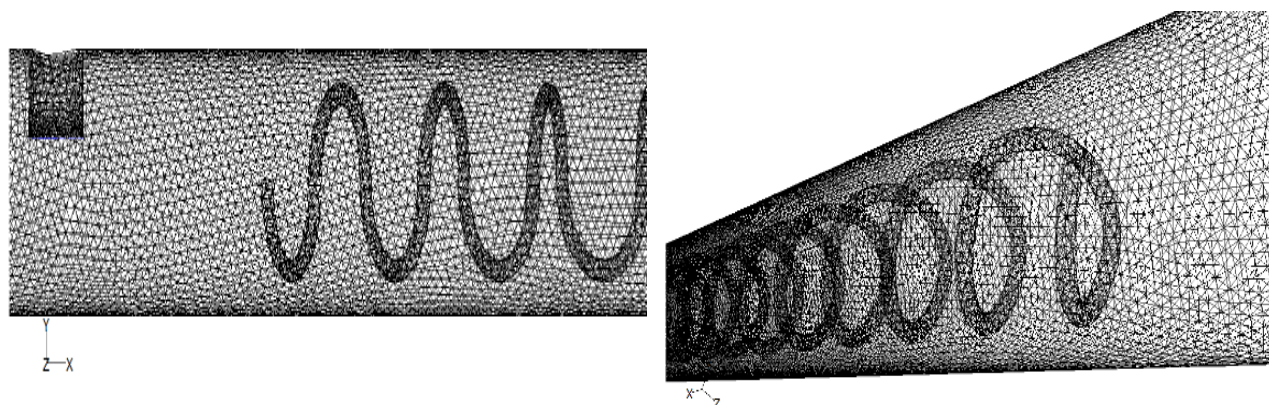


Figure 2. Schematic of the generated meshed for the pilot-scale pipeline.

Simulation was done for laminar state based on the experimental operating conditions. The simple pressure-velocity coupling, the standard pressure and the first-order upwind discretization schemes were used for pressure-velocity coupling. In addition, a convergence criterion of 10^{-6} was considered in the modeling. Also, the mercaptan removal reaction was considered in the modeling. A first-order kinetics with a global kinetic constant of $K (25\text{ }^{\circ}\text{C}) = 22.6\text{ h}^{-1}$ and a global activation energy of $48.4\text{ kcal.mol}^{-1}$ were used for the non-catalytic oxidation reaction in the presence of sodium hydroxide solution in the modeling based on literature reviews [14].

4. Results and discussion

4.1. Experimental results

In order to study the effect of static mixer to improve the mixing quality of mercaptan removal from the untreated Kerosene, experiments were carried out using four described mixers as well as without a mixer at three flow rates of Kerosene, including 2, 18 and 30 mL/s. The initial value of mercaptan in the kerosene was determined as 135 ppm. The mercaptan measured concentration for three cases of mixers at different Kerosene flow rates and two elements of pitch of 1 and 3mm are presented in Tables 1 and 2, respectively.

Table 1

Measured concentration of mercaptan for three states of mixers at different Kerosene flow rates for elements pitch of 1 mm.

| Flow rate (mL/s) | Concentration of mercaptan (ppm) | | |
|------------------|----------------------------------|---------------------|---------------------|
| | without mixer | mixer length= 20 cm | mixer length= 40 cm |
| 2 | 115 | 105 | 96 |
| 18 | 119 | 111 | 104 |
| 30 | 130.5 | 118 | 113 |

Table 2

Measured concentration of mercaptan for three states of mixers at different Kerosene flow rates for elements pitch of 3 mm.

| Flow rate (mL/s) | Concentration of mercaptan (ppm) | | |
|------------------|----------------------------------|---------------------|---------------------|
| | without mixer | mixer length= 20 cm | mixer length= 40 cm |
| 2 | 115 | 110 | 107 |
| 18 | 119 | 116 | 110 |
| 30 | 130.5 | 123 | 120 |

Fig. 3 shows the effect of the static mixer length on the mercaptan removal at different flow rates of Kerosene for elements of pitch 1 mm (a) and 3 mm (b). In order to do the mercaptan removal from the kerosene effectively, it is necessary to enhance the mixing between the caustic soda and kerosene stream. Therefore, it seems that using static

mixers is a suitable way to lead to a better mixing. This figure shows that the mercaptan concentration at the outlet of the line equipped with a static mixer is lower than the line without the static mixer. This indicates better performance of the mercaptan removal in the case of applying static mixer in comparison to the the case of no static mixer.

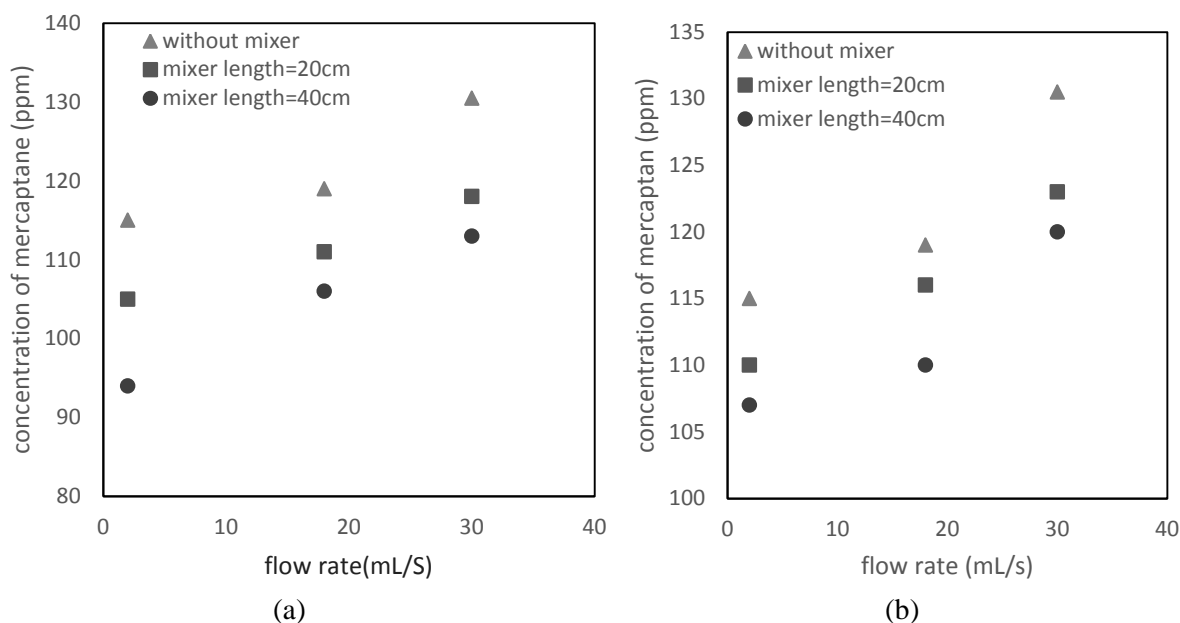


Figure 3. Effect of mixer length at various Kerosene flow rates on the mercaptan removal (a: 1 mm elements pitch, b: 3 mm elements pitch).

Also, the mercaptan amount of the outlet stream will decrease as the mixer length increases. So, 40 cm in length of static mixer has a better mercaptan removal performance than 20 cm in length of static mixer.

Similarly, variation of the measured

mercaptan for two mixers pitch at various Kerosene flow rates is shown in fig. 4 for cases of 20 cm (a) and 40 cm (b). As seen, if the mixer pitch decreases, the mercaptan concentration in the outlet stream decreases for all the examined Kerosene flow rates. It

can be concluded that mixer pitch of 1mm has a better performance in the mixing and removal of mercaptan. This is due to

increasing of turbulent at the lower mixer pitch.

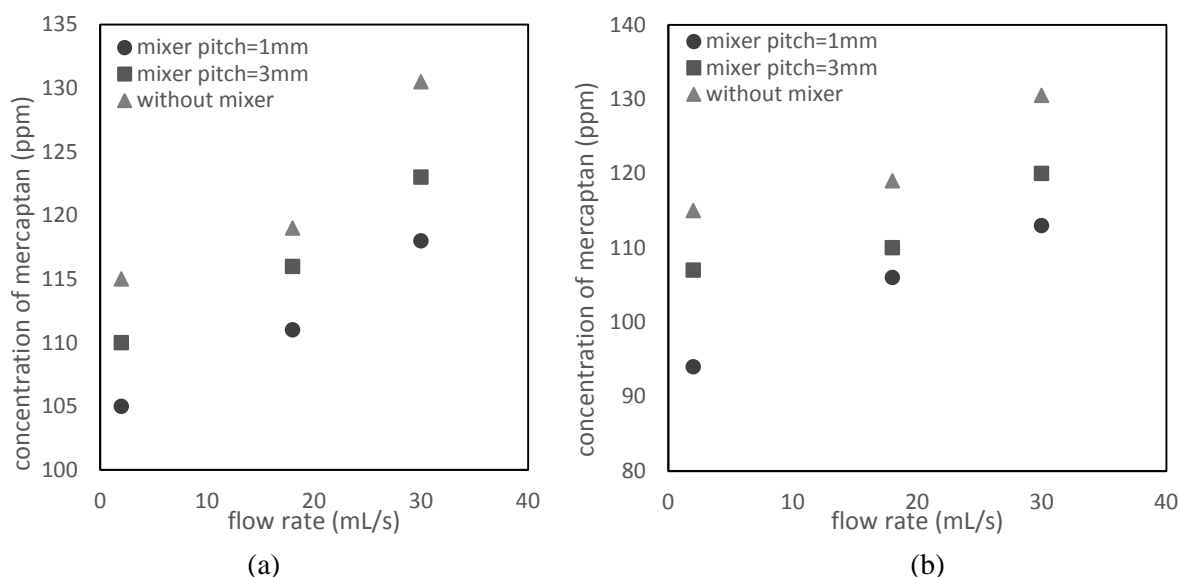


Figure 4. Effect of mixer pitch at various Kerosene flow rates on the mercaptan removal (a: mixer length= 20 cm, b: mixer length= 40 cm).

The experimental results show higher concentration of the mercaptan in the outlet stream at higher flow rates of Kerosene. As the flow rate of the main stream increases, the residence time of the fluid in the line will decrease that resulted in poor mixing progress and mass transfer between the caustic soda and Kerosene. Consequently, lower removal reaction performance will occur that causes higher mercaptan concentration at the outlet of the line. In all cases, the flow rate of 2 ml/s shows a greater effect on the reaction and mercaptan removal.

4.2. CFD modelling results

Computational Fluid Dynamics modeling was carried out to study the mixing performance in the pipeline in different operational conditions. In order to better illustrate mercaptan removal performance, the mixing progress was modeled in different performed experimental conditions.

Pilot-scale system equipped by a static

mixer of length 20 cm was modeled and the Kerosene and caustic soda were used as the working fluids. Three levels of the streams, including low mean and high levels, were considered like the experimental tests in a way that the ratio of Kerosene flow rate to the injected caustic soda was fixed equal to 24 in all conditions.

Fig. 5 shows the velocity contours at a longitudinal slice as well as four different vertical cross-sections along the pilot-scale pipe line for three considered operational conditions. Cross-sections 1 and 2 are related to the region of the line equipped by the static mixer, and cross-sections 3 and 4 are related to rest of the line without static mixer. It can be seen in this figure that as the flow rate of the caustic soda and kerosene stream increases simultaneously, the velocity magnitude will increase along the line. Another outstanding point in this figure is that at mean and high flow rates, a uniform contour is observed after the mixer region.

This indicates that a suitable mixing has been achieved in the static mixer region for these operational conditions.

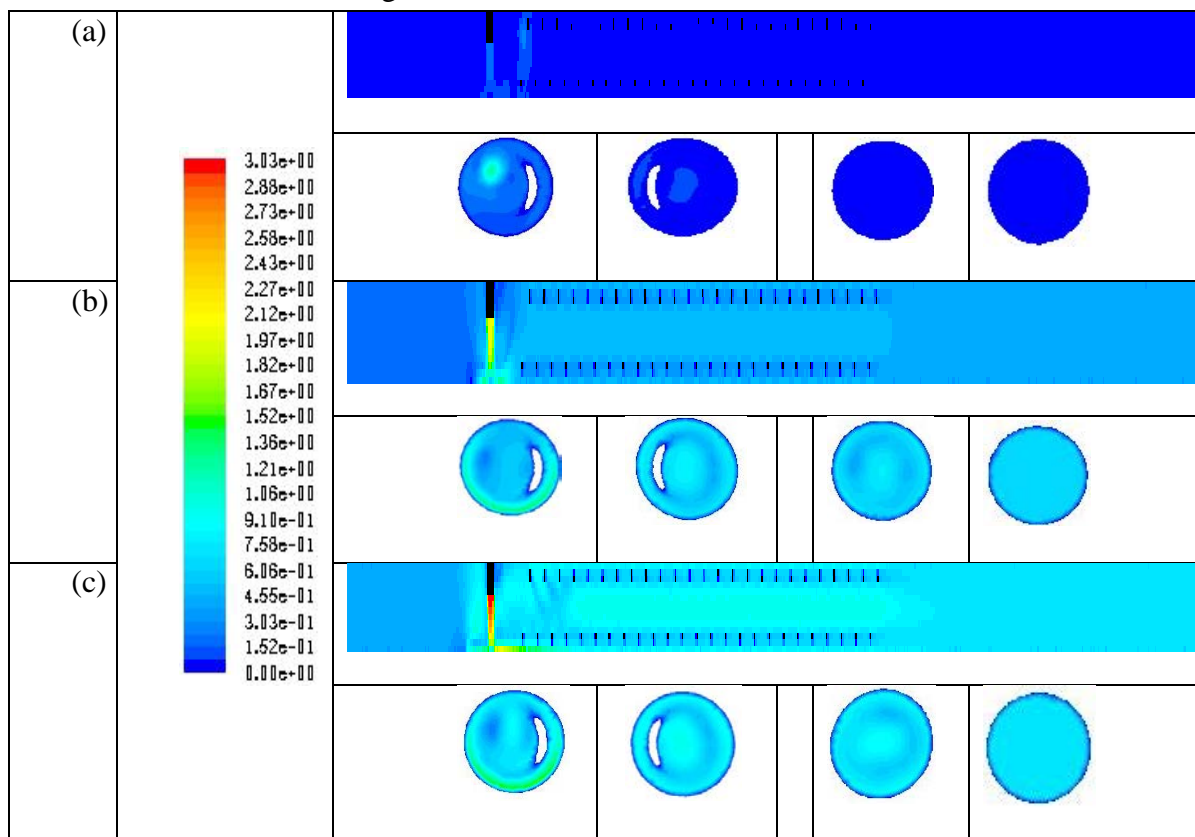


Figure 5. Contours of velocity along the line at various levels of the kerosene and caustic soda flow rates (a: low flow rates, b: mean flow rates, c: high flow rates).

Quantitative comparison of velocity magnitude along the line is shown in Fig. 6. The velocity magnitude is about 0.05 m/s along the line at the low level of the caustic soda and Kerosene flow rates. The velocity magnitudes are about 0.5 and 1 m/s for the mean and high levels of flow rate at the

region equipped by the mixer. These magnitudes were reduced to 0.4 and 0.8 m/s in the region without mixer for the mean and high levels, respectively. Higher velocity magnitude in static mixer region causes sufficient mixing in this region and thus better removal performance.

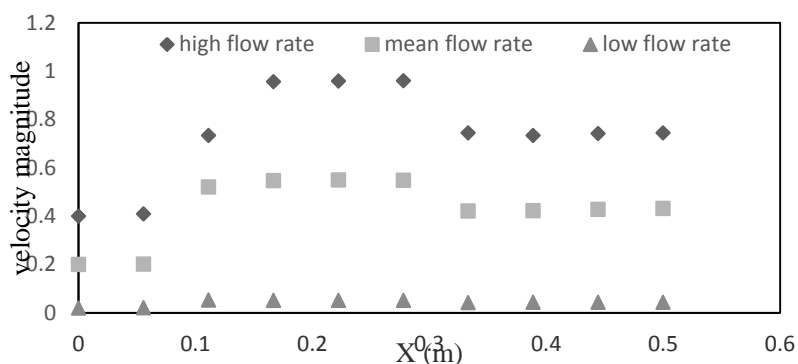


Figure 6. Variation of the velocity magnitude along the line at different levels of the Kerosene and caustic soda flow rates.

As mentioned, mercaptan will be oxidized and converted to disulfide in the line. This process has been modeled based on the explained reactions. To evaluate the mercaptan removal reaction performance, mass fraction contours of mercaptan (RSH) as the reactant and disulfide (RSSR) as the product at different flow rates are presented in figures 7 and 8, respectively.

Comparison between contours of RSH at different cross-sections show that the mass fraction of RSH at higher flow rates is higher than that at lower flow rates of the main and

injected streams, indicating that the reactants have sufficient residence time and mercaptan will be converted to disulfide in a better way at lower flow rates. Also, it can be seen that contours of RSSR mass fraction at lower flow rates are higher than their fractions at higher flow rates.

It should be mentioned that sufficient residence time has an important role in the performance of mercaptan removal reaction in the line. So, lower flow rates resulted in higher residence time show a better performance of the removal reaction.

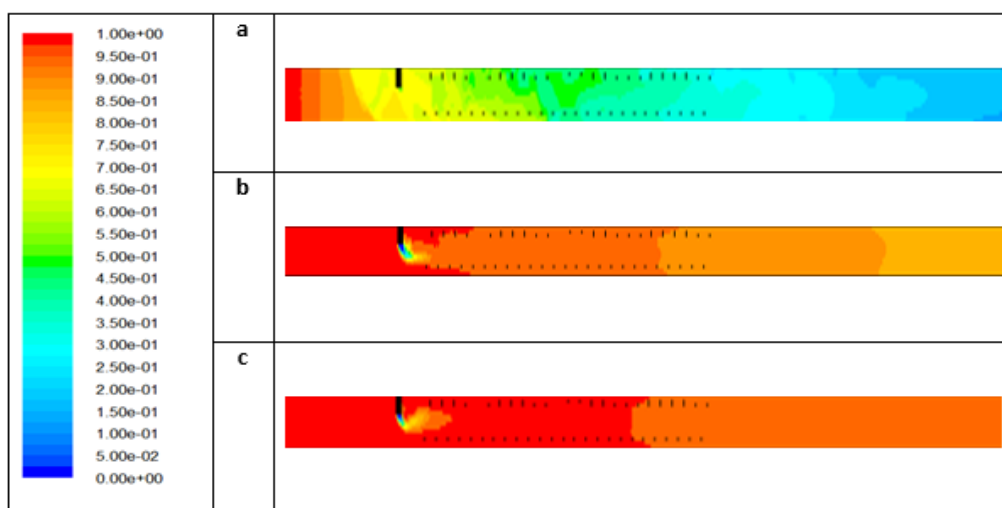


Figure 7. Contours of mass transfer of RSH along the line at various levels of the Kerosene and caustic soda flow rates (a: low flow rates, b: mean flow rates, c: high flow rates).

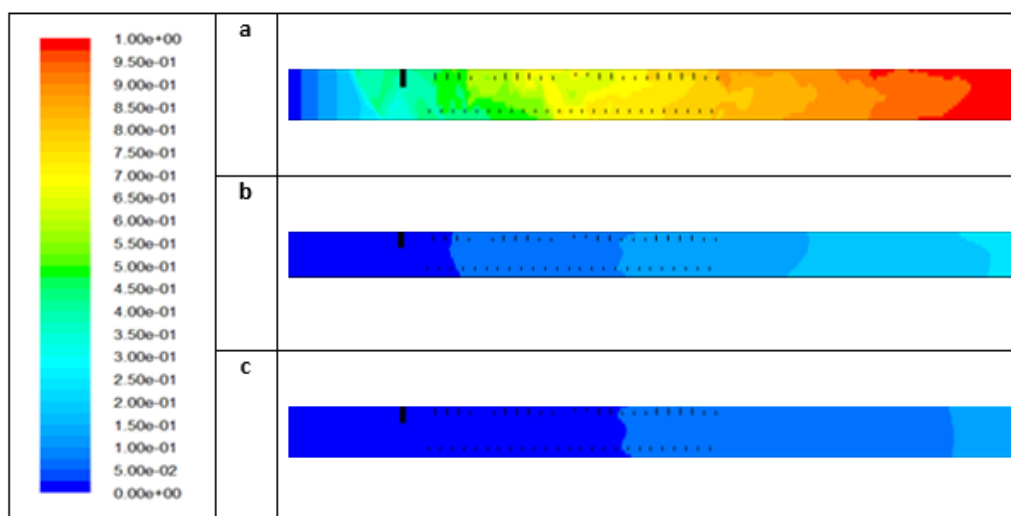


Figure 8. Contours of mass transfer of RSSR along the line at various levels of the Kerosene and caustic soda flow rates (a: low flow rates, b: mean flow rates, c: high flow rates).

5. Conclusions

Static mixers are used instead of mechanically agitated vessels due to their advantages such as the small space requirement, low equipment cost, short residence times, and good mixing at low shear rates. In order to study the effects of mixer length, mixer pitch at various flow rates of Kerosene on the mercaptan removal, four mixers with lengths of 20 cm and 40 cm and pitches of 1mm and 3mm at three flow rates of 2, 18 and 30 mL/s were examined. Results show that using static mixer is a good way to improve the mixing quality. At a fixed Kerosene's flow rate, effective removal of the mercaptan in the pilot line will be achieved as the length of the static mixer increases and its elements of pitch decrease. Also, the mercaptan removal reaction is taken place in a better way at lower flow rates. This is due to sufficient residence time of the feed in the line that causes better removal reaction. In the CFD modelling, it was observed that the higher mass transfer rate occurred at the region equipped by the mixer due to the higher mixing quality. Also, lower flow rate in static mixer region causes sufficient mixing in this region and thus better removal performance.

Nomenclature

| | |
|-------------|--|
| K | kinetic constant [h^{-1}]. |
| P | pressure [Nm^{-2}]. |
| S | source term. |
| U | velocity vector [ms^{-1}]. |
| u, v, w, | mean velocity components [ms^{-1}]. |
| u_i, u_j | |
| $u', v',$ | turbulent fluctuating velocity |
| $w', u_i',$ | component [ms^{-1}]. |
| u_j' | |
| x_i, x_j | Cartesian coordinate [m]. |

Greek symbols

| | |
|-------|---|
| μ | laminar, turbulent and effective viscosities [Pas]. |
|-------|---|

| | |
|---------------|---|
| ρ | density [kg m^{-3}]. |
| Φ, ϕ' | mean and turbulent fluctuating values of scalar property. |
| Γ | scalar diffusion coefficient. |

Subscripts

| | |
|------|------------|
| i, j | component. |
|------|------------|

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