Novel Type of Four-Impinging-Jets Reactor for Oxidative Desulfurization of Light Fuel Oils

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A novel type of four-impinging-jets reactor (FIJR) has been proposed and tested successfully for the oxidative desulfurization of kerosene as a typical light fuel oil. The FIJR is characterized by a high-intensity mixing chamber located at the bottom of the reactor and equipped with four impinging jets. The influences of various operating and design parameters such as feed flow rate, internozzle distance, jet diameter, and jet Reynolds number on the performance of the FIJR have been carefully investigated. As a result of both the impinging process and shear forces exerted on the phases, the rate of desulfurization in FIJR increased significantly compared to that obtained by a conventional reactor system such as stirred-tank reactor (STR). This can be attributed to a decrease in the mass-transfer resistance, complex flow pattern within the reaction chamber, energy released as the result of impinging-jets collision, and high intensity mixing at the impingement zone of FIJR. Moreover, about 92% sulfur removal of kerosene has been obtained in FIJR.

1. Introduction

Sulfur-containing compounds of middle distillate fuels, which are converted to SO_x in combustion, are the major source of acid rain and air pollution. Thus, new environmental concerns necessitate low sulfur content of hydrocarbon-based middle distillate fuels.[1-6] At present, the conventional industrial process for removing sulfur-containing compounds from middle distillate fuels is hydrodesulfurization (HDS). Although HDS is highly efficient in removing thiols, sulfides, and disulfides, it is less effective for thiophenic compounds as the main sulfur-containing compounds of middle distillate fuels in the boiling range of kerosene and gas oil.[4] To meet new sulfur standards with HDS process, operation at higher temperature, higher pressure, and more active catalysts is indispensable and, hence, requires higher investment and operating cost. Therefore, several new processes have been developed to remove satisfactorily these refractory sulfur-containing compounds such as biodesulfurization,[7,8] selective adsorption,[9] oxidative desulfurization (ODS),[10] etc.

The ODS process has recently received much attention for desulfurization of middle distillates because of its two main advantages relative to the HDS process. The first advantage of the ODS process is the fact that it can be carried out in the liquid phase and under very mild temperature and pressure conditions. The second advantage is high reactivity of HDS refractory sulfur-containing compounds (e.g., thiophenic compounds and its alkylated derivatives) toward oxidation by this method. In other words, the ODS process has complementary chemistry to the HDS process. In the ODS process, the sulfur-containing compounds are oxidized to their corresponding sulfoxides and subsequently sulfones readily. Afterward, these polar products can be removed by a number of conventional separation processes such as solvent extraction, adsorption, etc.[4,10-12]

Various types of oxidants and catalysts have been examined for the ODS process. Oxidants used include hydrogen peroxide,[11-17] nitric acid,[18,19] nitrogen oxides,[20] organic hydrop-eroxides (e.g., *tert*- butyl hydroperoxide),[21-25] ozone,[26] air,[27] potassium ferrate (K_2FeO_4),[28] Fenton's reagent,[29] etc. On the basis of the available literature on the oxidative desulfurization, one can easily classify the oxidation systems as follows:[10] (1) two-liquid-phase oxidation system using aqueous hydrogen peroxide as oxidant, (2) single-liquid-phase oxidation system using organic hydroperoxide, and (3) gas−liquid phase oxidation system. A large number of reports can be found regarding the first group. The main reasons for the use of hydrogen peroxide as the oxidizing agent are its (1) low cost, (2) nonpolluting and environmental friendliness, (3) not strongly corrosive, and (4) commercial availability. Hydrogen peroxide in the presence of catalysts such as acetic acid,[3,16,30,31] formic acid,[13-15,32,33] polyoxomethalate,[13] Ti-HMS/TS-1[34] has been used. However, different solid basic catalysts such as polymolybdates supported on alumina,[35] V_2O_5/Al_2O_3 and V_2O_5/TiO_2,[36,37] Co−Mo/Al_2O_3,[38] and Mo/Al_2O_3[39] have also been used. Among different oxidation systems in the category of the two-phase-oxidation systems, hydrogen peroxide with carboxylic acids (e.g., formic acid), which produce in situ peracid (i.e., performic acid) has several advantages over other oxidation systems. These advantages are commercial availability of formic acid as the catalyst, simplicity of oxidation system, and no need for solid catalyst and solvent in the oxidation media. Although there are several papers and patents in the field of ODS of middle distillates using hydrogen peroxide and formic acid oxidation system, these reports mainly focused on the chemistry of the process, and the engineering aspects such as reactor design of the process are not studied well.

The impinging-jets (IJ) technique has a unique flow configuration. The first patent regarding this technique may be published by Bower.[40] The IJ method was used by Elperin[41] for gas−solid suspensions and further developed by Tamir[42] for various chemical engineering processes. The IJ technique has been successfully applied to various chemical processes such as desorption,[43] absorption,[44-47] solid−liquid enzyme reactions,[48,49] copper extraction and stripping,[50,51] liquid−liquid reactions,[52,53] liquid−liquid extraction,[54] catalytic wet peroxide oxidation of phenol,[55] precipitation,[56,57] and crystallization,[58] drying,[59,60] and mixing.[61-66]

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Table 1. Properties of Kerosene Feedstock

property	value	test method
density (kg/m³)	795	
viscosity at 20 °C (mPa·s)	1.46	
total nitrogen (ppmw)	6.2	ASTM D-3228
total sulfur (ppmw)	2335.0	ASTM D-4294
aromatics (vol %)	15.85	ASTM D-1319
paraffins (vol %)	60	ASTM D-1319
naphthenes (vol %)	22.61	ASTM D-1319
olefins (vol %)	1.54	ASTM D-1319
total acid number (mg KOH/g)	0.018	
distillation range (°C)		
initial boiling point (IBP) (°C)	173	ASTM D-86
5%	179	
10%	183	
30%	195	
50%	209	
70%	225	
90%	245	
95%	254	
final boiling point (FBP) (°C)	269	

In the present work, first, some preliminary oxidation experiments were carried out to find the appropriate oxidation conditions for the ODS of kerosene. Then, the obtained appropriate operating conditions were used as oxidation conditions in the operation of a new type of four-impinging-jets reactor. Therefore, the major goal of the present work was to propose and test the performance capability of a new type of four-impinging-jets reactor for the ODS of nonhydrotreated kerosene as a typical light fuel oil with high total sulfur content.

2. Experimental Section

2.1. Chemicals. Chemicals used in the present investigation such as formic acid (>99%), acetonitrile, and hydrogen peroxide (30 wt %) were of analytical grade, obtained from Merck Co. (Germany), and used as received without any treatment. Nonhydrotreated kerosene as a feedstock with a total sulfur content of 2335 ppmw and the specifications summarized in Table 1 was obtained from Tehran refinery (Tehran, Iran). The health and safety issues concerning the chemicals used in the present study can be found elsewhere.[67]

2.2. Method of Analysis. Agilent 6890 series gas chromatograph system with Agilent 5973 network mass selective detector and capillary column DB-1 ms (100% dimethyl polysiloxane, 30 m, length × 0.25 mm, i.d. × 0.25 μm, film thickness) was used to detect sulfur-containing compounds in kerosene qualitatively. The injector temperature was set to 250 °C in split mode with split ratio of 20. The initial temperature was set to 50 °C for 5 min and then the temperature was increased to 275 °C with temperature increasing at a rate of 5 °C/min and then kept constant at 275 °C for 10 min.

A Chrompack CP 9000 gas chromatograph equipped with a flame photometric detector (GC-FPD) was used to compare the chromatograms of sulfur-containing compounds in untreated original kerosene with those of the treated kerosene. A fused-silica capillary column (CP-Sil 8 CB, from Supelco Company, 30 m, length × 0.320 mm, i.d. × 0.25 μm, film thickness) was used for separation. The injector and detector temperatures were set to 270 and 300 °C, respectively, while the detector was fed with 142 mL/min of hydrogen, 75 mL/min of air₁ (the primary air-H₂ flame for combustion purposes), and 166 mL/min of air₂ (the secondary air-H₂ flame for photometric detection). The GC split valve was opened with the split ratio of 1:150 and nitrogen was used as carrier gas with a constant column flow rate of 0.5 mL/min. The column temperature programming was as follows: the oven temperature was set at 100 °C for 3 min, then increased

to 275 °C with a rate of 5 °C/min and kept constant at 275 °C for 10 min. Finally, 1 μL of the sample was injected into the GC-FPD for analysis.

The total sulfur content of all kerosene samples with a total sulfur content higher than 990 ppmw were determined by SLFA-20 sulfur in oil analyzer (Horiba, USA). SLFA-20 has the total sulfur range of 0 to 5 wt %, with a lower detection limit of 20 ppm, and the test method is based on ASTM D 4294. The total sulfur content of treated kerosene samples with the total sulfur content lower than 990 ppmw were determined using a more precise analyzer, for instance, FX-700 sulfur analyzer (Tanka, Japan). The analyzer has a total sulfur range of 0−990 ppmw, with a lower sulfur detection limit of 1 ppm. The test method is based on the wavelength dispersive X-ray fluorescence technique according to the ASTM D 2622. All total sulfur measurements were performed by the central laboratory of Esfahan refinery (Esfahan, Iran). General properties of kerosene such as aromatic content, total acid number, etc. were determined by central laboratory of Esfahan refinery according to corresponding ASTM methods.

The concentration of hydrogen peroxide in the aqueous phase of oxidation media before and after the oxidation reaction has been determined using volumetric titration with sodium thiosulfate (Na₂S₂O₃) standard solution and an excess amount of KI in an acidic medium.

It is important to note that for each data point, the experimental runs were repeated two times and thus each data point was determined based on the mean value of at least two measurements with a standard deviation of 2−4%.

2.3. Experimental Setup and Procedures. 2.3.1. Preliminary Oxidation Experiments. In each oxidation run, 50 mL of untreated kerosene with a total sulfur content of 2335 ppmw was introduced into a 250-mL three-necked glass reactor equipped with a condenser and a thermometer. The reactor was placed in a constant-temperature water bath to adjust the temperature of solution with an accuracy of ±1 °C. Then, the desired amount of formic acid according to preset acid to sulfur molar ratio (acid/S) was added to the reactor. The reaction mixture was rigorously stirred and heated to the desired temperature. Afterward, an appropriate amount of hydrogen peroxide according to preset oxidant to sulfur molar ratio (O/S) was added to the reaction mixture and, this time, was recorded as the initial time of the reaction. The reaction time was set to 120 min. After 120 min, the stirring was stopped and the aqueous and hydrocarbon phases were decanted in a separatory funnel. The hydrocarbon phase (i.e., oxidized kerosene) was washed with 100 mL of distilled water in order to remove any entrained aqueous phase. The oxidized kerosene was extracted by means of acetonitrile according to the extraction procedure.

2.3.2. Extraction Procedure. In the extraction stage, oxidized kerosene with an appropriate amount of acetonitrile according to the solvent/kerosene ratio of 0.5 were charged into a 250 mL flat-bottom flask. The flask was then placed in a constant-temperature water bath, and the mixture was vigorously stirred for 10 min at 25 °C. The dispersion formed was then allowed to separate into two distinct phases (i.e., aqueous and hydrocarbon phases) in a separatory funnel. The aqueous phase was removed and the above procedure was followed again for the hydrocarbon phase. Finally, after second stage of extraction, the hydrocarbon phase (i.e., treated kerosene) was washed with distilled water two times and dried over magnesium sulfate in order to remove the water content of treated kerosene. The treated kerosene was analyzed for the total sulfur content measurements.

(a) FIJR experimental set up
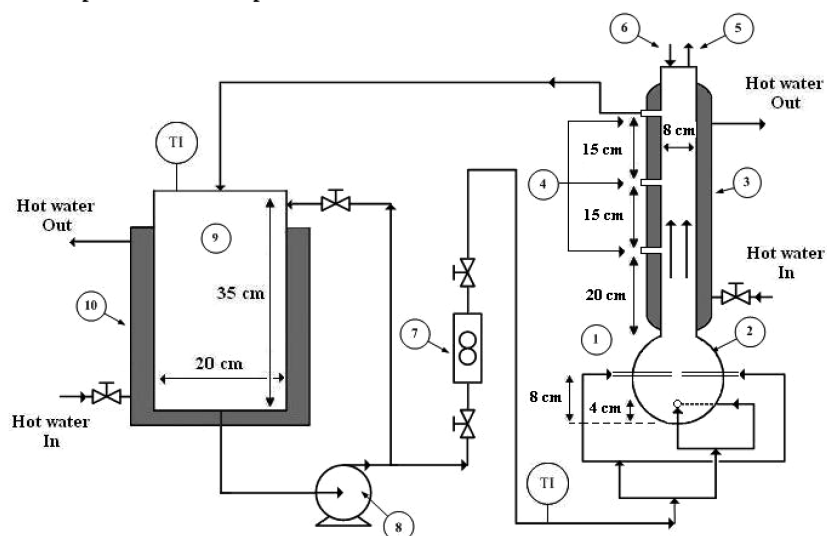
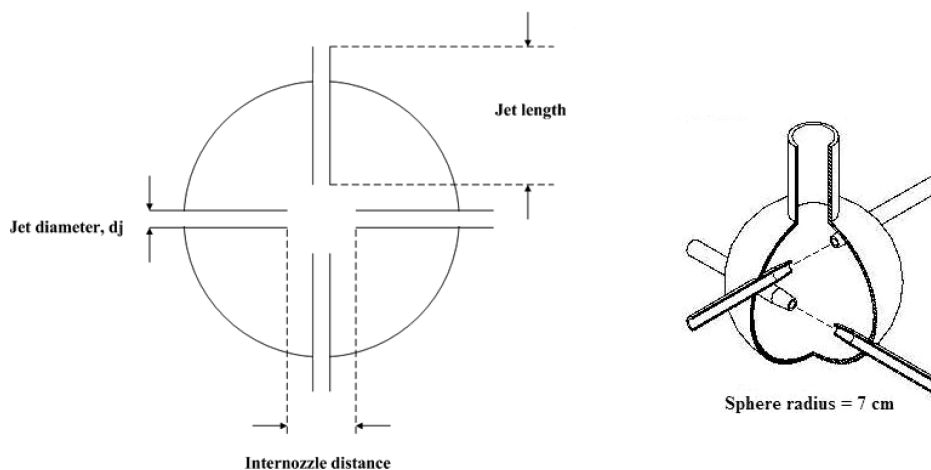**(b) Jet impingement configuration**

Top view

Figure 1. Experimental setup of FIJR: (1) four-impinging-jets reactor; (2) mixing zone; (3) hot water jacket; (4) outlet ports; (5) sampling connection; (6) formic acid, H_2O_2 entering connection; (7) rotameter; (8) stainless steel feed pump; (9) stainless steel feed vessel; (10) hot water jacket.

2.3.3. Four-Impinging-Jets Reactor (FIJR). The flow diagram of the experimental setup shown in Figure 1 consisted of the following parts: four-impinging-jets reactor (FIJR) whose dimensions are specified in Figure 1 (1); mixing zone equipped with four identical nozzles (2); hot water jacket of reactor (3); outlet ports (4); sampling connection (5); formic acid and hydrogen peroxide entering connection (6); rotameter to adjust the feed flow rate (7); stainless steel feed pump (8); stainless steel feed vessel (9); hot water jacket of feed vessel (10). In each experimental run, 7.0 L of kerosene with a total sulfur content of 2335 ppm was introduced into the feed vessel. The kerosene in the feed vessel was heated to 60 °C. Then, 459 mL of formic acid was introduced into the reactor through the upper connection of FIJR. This amount of formic acid is almost equal to acid/S = 30. Afterward, 207 mL of hydrogen peroxide was added to the reactor through the upper connection of FIJR. This amount of hydrogen peroxide is almost equal to O/S = 5. Then, the kerosene with specified volumetric flow rates was fed to the mixing zone of the reactor through 4 identical nozzles located at the middle and bottom of the reaction chamber. The liquid jets exiting the opposed nozzles collide with each other

in the reaction chamber. The hydrocarbon phase after passing through the upper part of the reactor recycled to the feed vessel. The samples were taken through the sampling connection according to predefined time intervals with a syringe. The oxidized kerosene samples were then extracted according to the extraction procedure.

It should be also mentioned that according to our previous experience, the appropriate geometry for reaction chamber is a spherical geometry to prevent creating dead zone and to make prefect mixing. The volume of the reaction chamber (about 1400 mL) was chosen twice the volume of the oxidant/acid mixture (about 700 mL) to make sure that the major fraction of the aqueous mixture remains in the chamber. The upper part of the reactor called gravity settler was equipped with 3 outlet ports to make the reactor more flexible in order to achieve complete phase separation by choosing the appropriate outlet port. Note that the main propose of the upper part of the reactor system is to prevent circulation of entrained droplets of aqueous phase (i.e., formic acid and hydrogen peroxide) to the feed vessel. In fact, the upper part of reactor is a gravity settler that lets the
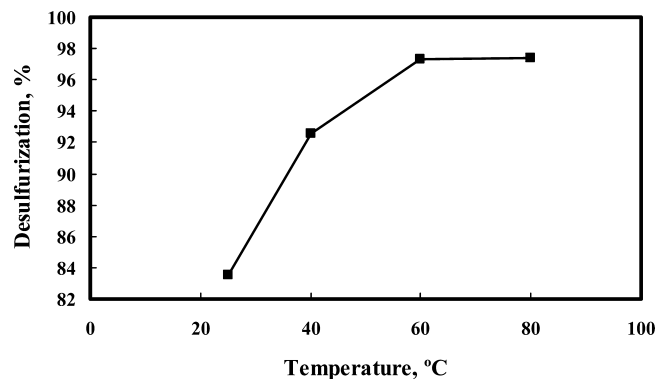
Figure 2. Experimental setup of STR: (1) stirred-tank reactor; (2) variable speed motor; (3) heater; (4) formic acid, H_2O_2 entering connection and sampling connections (5) aqueous phase recycle connection; (6) baffle; (7) gravity settler; (8) aqueous phase recycle pump; (9) settler valve; (10) rotameter; (11) stainless steel feed pump; (12) feed vessel; (13) hot water jacket.

droplets of aqueous phase to disengage and keeps the aqueous phase in the mixing zone of FIJR.

2.3.4. Stirred-Tank Reactor (STR). To examine the performance capability of an STR, an experimental run was carried out with an STR as a conventional reactor for oxidative desulfurization of kerosene. A schematic diagram of STR used in the present investigation is shown in Figure 2. This set up consisted of the following parts: stirred-tank reactor (1); variable speed electric motor (2); heater (3); formic acid and hydrogen peroxide entering and sampling connections (4); aqueous phase recycle connection (5); baffles (6); gravity settler (7); aqueous phase recycle pump (8); settler valve (9); rotameter to adjust the feed flow rate (10); stainless steel feed pump (11); feed vessel (12); hot water jacket (13). The reactor was equipped with a variable speed standard six-flat blades turbine-type stirrer and four baffles. The STR was designed in such a way that the volume of the mixing zone was the same as that of the FIJR. Besides, the total volume of mixing zone and the gravity settler of STR is the same as FIJR. Therefore, contact time in STR and FIJR is identical. In each experimental run, 7.0 L of kerosene with a total sulfur content of 2335 ppm was introduced into the feed vessel. The kerosene was heated to 60 °C in the feed vessel. Then, 459 mL of formic acid was introduced into the reactor through upper connection of STR. This amount of formic acid is almost equal to acid/S = 30. Afterward, 207 mL of hydrogen peroxide was added to the reactor through the above-mentioned connection. This amount of hydrogen peroxide is almost equal to O/S = 5. Then, the stirring was started and this time was taken as the "zero time" for the experimental records. During the course of the reaction, liquid samples were taken from the reactor according to predefined time intervals with a syringe. The oxidized kerosene samples were then extracted according to the extraction procedure.

3. Results and Discussion

As can be observed from Table 1, the range of boiling point of kerosene used in the present work is from 173 to 269 °C.

According to the literature,[4,15,68] the main sulfur-containing compounds of middle distillate in the range of kerosene boiling points are benzothiophene and its alkylated derivatives and some mercaptans such as 1-octanethiol, 1,5-pentanedithiol, and 4-m-ethyl-thiophenol.[68] GC−MS analysis confirmed the presence of benzothiophene and its alkylated derivatives such as 2,5,7-trimethyl benzothiophene, 4,5,6,7-tetramethyl benzothiophene, and also 2-ethyl-4-methyl thiophene in the present kerosene.

3.1. Preliminary Oxidation Studies. In the ODS process, sulfur-containing compounds are oxidized to sulfoxides and subsequently sulfones. The polarity of these oxidized compounds is changed in such a way that they can be separated by a conventional process such as liquid−liquid extraction. The main operating conditions of the present oxidation system are temperature, hydrogen peroxide to sulfur molar ratio (O/S), formic acid to sulfur molar ratio (acid/S), and oxidation time. First, it is important to study the effect of each operating condition in detail to find out the appropriate operating conditions of the oxidation system. Therefore, preliminary oxidation studies are conducted in the present investigation as a first step. In what follows, these effects are presented and discussed.

3.1.1. Effect of Temperature. To examine the effect of reaction temperature on the performance of the desulfurization process, a number of oxidation experiments at 25, 40, 60, and 80 °C with the O/S = 5, acid/S = 30, and the oxidation time equal to 120 min were carried out. The variation of the desulfurization versus oxidation temperature is presented in Figure 3. As can be observed from this figure, a rise in the reaction temperature from 25 to 60 °C leads to an appreciable increase in the desulfurization. The desulfurization increases from 83.6% at 25 °C to 97.3% at 60 °C and then remains constant with further increase in the reaction temperature from 60 to 80 °C. This increase in the desulfurization with an increase in the reaction temperature from 25 to 60 °C can be explained by the increase in the oxidation reaction rate of different sulfur-containing compounds present in kerosene due to strong

Figure 3. Effect of reaction temperature on the desulfurization. Oxidation conditions: hydrogen peroxide−formic acid system; initial total sulfur content of kerosene = 2335 ppmw; reaction time = 120 min; O/S molar ratio = 5; acid/S molar ratio = 30 (i.e., 1.58 mL of H_2O_2 and 3.51 mL of formic acid were used for oxidation of 50 mL of kerosene). Extraction conditions: T = 25 °C; solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

dependence of the reaction rates on the reaction temperature. However, further increase in the reaction temperature increases the rate of unfavorable thermal decomposition of hydrogen peroxide to water and oxygen as well, which in turn limits the increase of the oxidation reaction rate of different sulfur-containing compounds. Therefore, the appropriate reaction temperature for the oxidation of the present feedstock is about 60 °C.

3.1.2. Effect of Hydrogen Peroxide to Sulfur Molar Ratio (O/S). The consumption rate of oxidant (i.e., hydrogen peroxide) in the ODS process, significantly affects the economy of the ODS process. It is therefore important to examine the effect of O/S molar ratio on the performance of the ODS process in order to keep O/S molar ratio as low as possible. According to the oxidation reaction, the stoichiometric ratio of hydrogen peroxide to sulfur is 2; however, hydrogen peroxide is usually used more than the stoichiometric ratio because of (1) transport limitations in two-liquid-phases reaction systems, and (2) the unfavorable (thermal) decomposition of hydrogen peroxide to water and oxygen. The influence of the oxidant to sulfur molar ratio (O/S) on the oxidation of sulfur-containing compounds present in kerosene was investigated at 60 °C, acid/S = 30, and reaction time = 120 min. Figure. 4 shows the variation of desulfurization versus O/S molar ratio. As can be observed, an increase in the O/S molar ratio from 1 to 5 leads to an increase in the final desulfurization from 72.4 to 97.3%; but further increase in the O/S molar ratio from 5 to 20 leads to a slight decrease in the final desulfurization from 97.3 to 96.9% and in fact has practically no effect on the desulfurization. Note that the increase in the desulfurization with an increase in the O/S molar ratio from 1 to 5 is expected. However, the slight decrease in the desulfurization with an increase in the O/S molar ratio higher than 5 can be explained by a subsequent decrease in the formic acid concentration in the aqueous phase. When the O/S molar ratio increases at a constant acid/S molar ratio, two contrary phenomena occur: (1) on the one hand, hydrogen peroxide concentration in aqueous phase increases, and (2) on the other hand, formic acid concentration in the aqueous phase decreases, which has a negative effect on the performance of the oxidation system due to the decrease of performic acid concentration, which is known as the main oxidizing agent in this ODS system. It seems that with an increase in the O/S molar ratio beyond 5, the latter effect becomes pronounced and, hence, the performance of the ODS system slightly decreases. There-
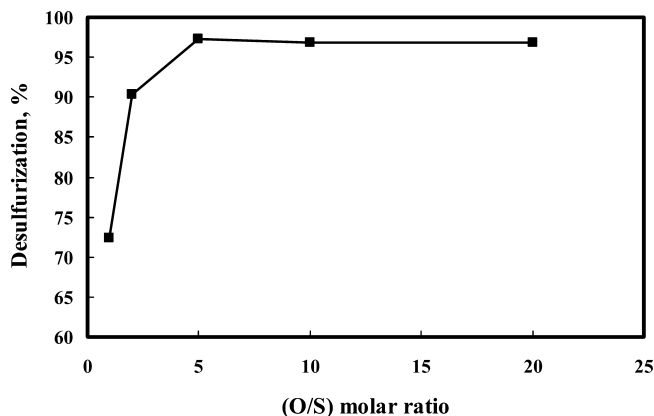
Figure 4. Effect of O/S molar ratio on the desulfurization. Oxidation conditions: hydrogen peroxide−formic acid system; T = 60 °C; initial total sulfur content of kerosene = 2335 ppmw; reaction time = 120 min; acid/S molar ratio = 30 (i.e., 0.32, 0.63, 1.58, 3.16, 6.33 mL of H_2O_2 for O/S molar ratio equal to 1, 2, 5, 10, 20, respectively, and 3.51 mL of formic acid were used for oxidation of 50 mL of kerosene). Extraction conditions: T = 25 °C; solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.
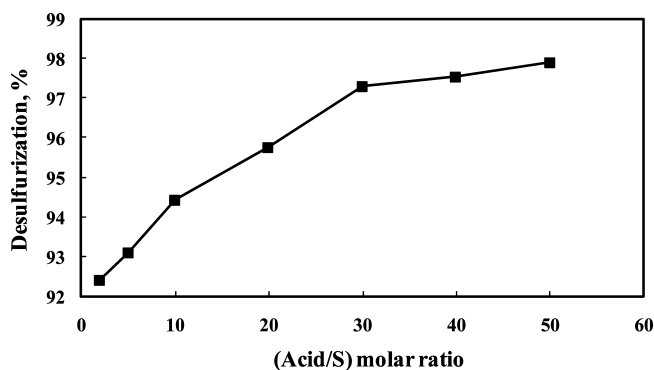
Figure 5. Effect of acid/S molar ratio on the desulfurization. Oxidation conditions: hydrogen peroxide−formic acid system; T = 60 °C; initial total sulfur content of kerosene = 2335 ppmw; reaction time = 120 min; acid/S molar ratio = 30 (i.e., 1.58 mL of H_2O_2 and 0.23, 0.59, 1.17, 2.34, 3.51, 4.68, 5.85 mL of formic acid for acid/S molar ratio equal to 2, 5, 10, 20, 30, 40, 50, respectively, were used for oxidation of 50 mL of kerosene). Extraction conditions: T = 25 °C; solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

fore, the appropriate O/S molar ratio for the ODS of the present feedstock is about 5.

3.1.3. Effect of Formic Acid to Sulfur Molar Ratio (Acid/S). The oxidation reaction can be promoted by increasing formic acid concentration via increasing performic acid, which is formed in situ by formic acid and hydrogen peroxide. In the present investigation, it was observed that desulfurization increases by increasing acid/S molar ratio. Figure 5 demonstrates the variation of desulfurization with acid/S molar ratio at 60 °C, O/S molar ratio equal 5, and reaction time equal 120 min. As can be observed from this figure, an increase in the acid/S molar ratio from 2 to 30 results in an increase in the desulfurization from 92.4 to 97.3% and further increase in acid/S molar ratio from 30 to 50 leads to only 0.6% increase in the desulfurization. This increase in the desulfurization with an increase in acid/S molar ratio can be explained by an increase in the performic acid concentration in the reaction medium, which in turn promotes the oxidation reactions. However, as it was reported previously by Hao et al.,[32] it seems that there is an equilibrium concentration for performic acid in the reaction mixture, and the concentration of performic acid cannot be increased beyond this equilibrium value with further increase
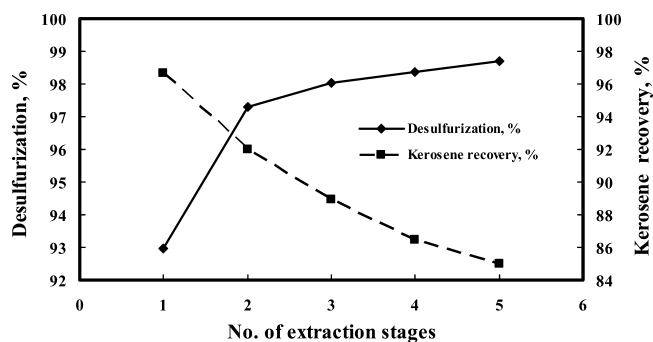
Figure 6. Effect of number of extraction stages on the desulfurization and recovery of kerosene. Oxidation conditions: hydrogen peroxide−formic acid system; initial total sulfur content of kerosene = 2335 ppmw; reaction time = 120 min; O/S molar ratio = 5; acid/S molar ratio = 30 (i.e., 1.58 mL of H_2O_2 and 3.51 mL of formic acid were used for oxidation of 50 mL of kerosene). Extraction conditions: T = 25 °C; solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

in the formic acid concentration. It is worth noting that formic acid is itself a good solvent for simultaneous extraction of oxidized sulfur-containing compounds in the oxidation media and desulfurization can be influenced due to this fact. Thus, the appropriate acid/S molar ratio for the ODS of the present feedstock is about 30.

3.1.4. Effect of Number of Extraction Stages. Number of extraction stages is an important factor in the extraction of oxidized sulfur-containing compounds. Generally, an increase in the desulfurization is expected with an increase in the number of extraction stages. However, in the separation of oxidized sulfur-containing compounds of kerosene, the solubility of kerosene in the solvent is a key parameter, because it affects the kerosene recovery after extraction. The dissolved hydrocarbon in extraction solvent can be recovered in solvent recovery stage by distillation. Nevertheless, it needs additional costs and, hence, selection of an appropriate extraction conditions for the separation of oxidized sulfur-containing compounds from kerosene is important. This is because it leads to an efficient extraction of oxidized sulfur-containing compounds with a low kerosene loss. Several extraction stages on the oxidized kerosene after oxidation with the appropriate operating conditions (i.e., temperature = 60 °C, O/S molar ratio = 5, and acid/S molar ratio = 30) were carried out. Figure 6 shows the desulfurization and kerosene recovery versus the number of extraction stages. As can be observed from Figure 6, for acetonitrile with solvent/kerosene ratio equal to 0.5, an increase in the number of extraction stages from 1 to 2, leads to an increase in the desulfurization from 93.0 to 97.3% and a decrease in the kerosene recovery from 96.7 to 92%. Moreover, further increase in the number of extraction stages from 2 to 5 leads to a small improvement in the desulfurization (i.e., only from 97.3 to 98.7%) but leads to a significant decrease in the kerosene recovery from 92% to 85%. Therefore, two-stage extraction was selected as appropriate number of extraction stages in the present work.

3.1.5. Effect of Reaction Time. Figure 7 shows the desulfurization of kerosene versus time under the appropriate operating conditions (i.e., temperature = 60 °C, O/S molar ratio = 5, acid/S molar ratio = 30, and number of extraction stages = 2). As can be observed, the main desulfurization happened at oxidation times below 60 min (from 0 to 96.5%) and increasing the reaction time from 60 to 240 min only leads to an increase in the desulfurization from 96.5 to 97.3%. Therefore, increasing the oxidation time over 60 min has no considerable effect on the final desulfurization.
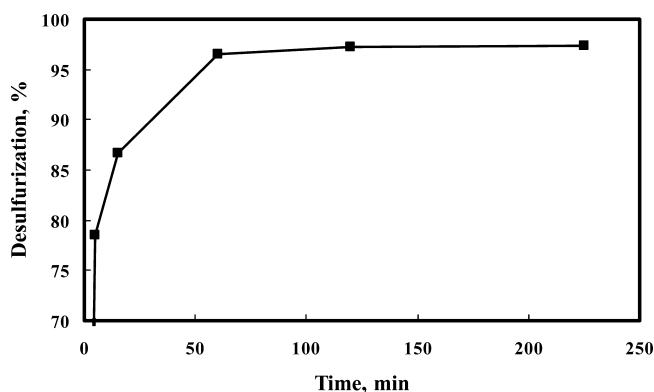

Figure 7. Desulfurization versus time of oxidation. Oxidation conditions: hydrogen peroxide−formic acid system; Initial total sulfur content of kerosene = 2335 ppmw; O/S molar ratio = 5; acid/S molar ratio = 30 (i.e., 1.58 mL of H_2O_2 and 3.51 mL of formic acid were used for oxidation of 50 mL kerosene). Extraction conditions: T = 25 °C; solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

3.1.6. Appropriate Operating Conditions of the ODS Process. The main operating conditions of the ODS process are oxidation temperature, hydrogen peroxide to sulfur molar ratio (O/S), formic acid to sulfur molar ratio (acid/S), reaction time, and the number of extraction stages after oxidation. Each operating condition was studied in the preliminary oxidation step. From these studies, it is found that the appropriate operating conditions of the ODS process are oxidation temperature equal to 60 °C, O/S = 5, and acid/S = 30. It is also important to note that an increase in the oxidation time over 60 min has practically no effect on the desulfurization. Besides, increasing the number of extraction stages greater than 2 may lead to higher kerosene loss without a noticeable increase in the final desulfurization.

Therefore, these operating conditions were used as the ODS process conditions in the operation of proposed FIJR. Note that when O/S = 5 and acid/S = 30 were used in the oxidation media, the initial concentration of hydrogen peroxide in the aqueous phase of oxidation media was determined to be 3.04 M (mol/L) and the remaining hydrogen peroxide concentration in the aqueous phase after oxidation reactions was also determined to be 0.172 M. Figure 8 shows the comparison of the GC-FPD chromatograms of the untreated kerosene with kerosene treated by the present ODS process at the above-mentioned-process conditions. As can be observed, the peaks of sulfur-containing compounds were diminished in the treated kerosene. Table 2 shows the properties of kerosene after ODS treatment.

As can be observed, the distillation characteristics of kerosene as one of the major properties of the kerosene feedstock remain practically unchanged. The acidity of kerosene, which is denoted by total acid number, is approximately the same before and after treatment by the ODS process. It should be noted that, despite using formic acid as the catalyst in the ODS process, the acidity of kerosene is not changed practically. Besides, as can be observed from Table 2, the aromatic content of kerosene decreases from 15.85% to 10.94 vol. %, which is equivalent to 30.0% dearomatization of the kerosene. But other hydrocarbon parts of kerosene (i.e., paraffins, olefins, and naphthens) remained practically unchanged and the observed increase in naphthene and olefin content of treated kerosene are due to dearomatization of kerosene.

3.2. Oxidative Desulfurization in Four-Impinging-Jets Reactor (FIJR). It is important to mention that two-jets configuration (TIJR) has been tested in our preliminary studies, but the mixing in TIJR was not satisfactory and some of the
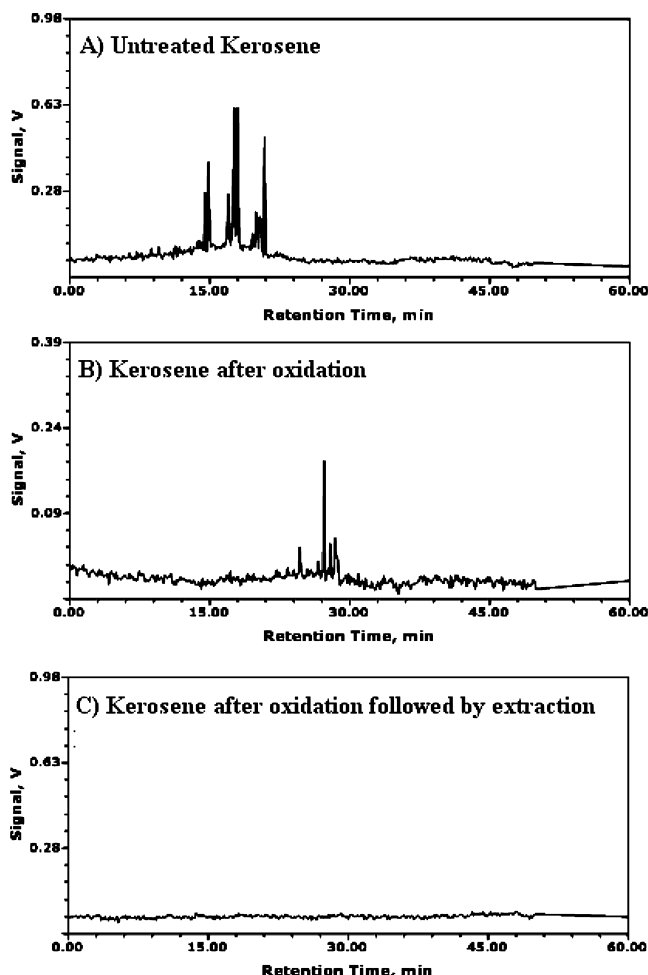
Figure 8. GC-FPD chromatograms of untreated and treated kerosene: (A) untreated kerosene; (B) kerosene after oxidation, (C) kerosene after oxidation followed by extraction. Oxidation conditions: hydrogen peroxide−formic acid system; initial total sulfur content of kerosene = 2335 ppmw; reaction time = 120 min; O/S molar ratio = 5; acid/S molar ratio = 30 (i.e., 1.58 mL of H_2O_2 and 3.51 mL of formic acid were used for oxidation of 50 mL of kerosene) Extraction conditions: T = 25 °C, solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

Table 2. Properties of Kerosene Feedstock before and after Treatment

property	before treatment	after treatment
density (kg/m³)	795	787
viscosity at 20 °C (mPa·s)	1.46	1.75
aromatics (vol %)	15.85	10.94
paraffins (vol %)	60	58.8
naphthenes (vol %)	22.61	28.64
olefins (vol %)	1.54	1.62
total acid number (mg KOH/g)	0.018	0.019
initial boiling point (IBP) (°C)	173	177
5%	179	181
10%	183	186
30%	195	196
50%	209	210
70%	225	226
90%	245	247
95%	254	257
final boiling point (FBP) (°C)	269	269

aqueous phase remained unmixed on the bottom of mixing zone and the performance was not satisfactory even at high Reynolds numbers (the desulfurization achieved in two-jets configuration was only 72%). Therefore, four-impinging-jets reactor (FIJR) was proposed and tested in the present investigation. It is important to note that the performance of the reactor increases
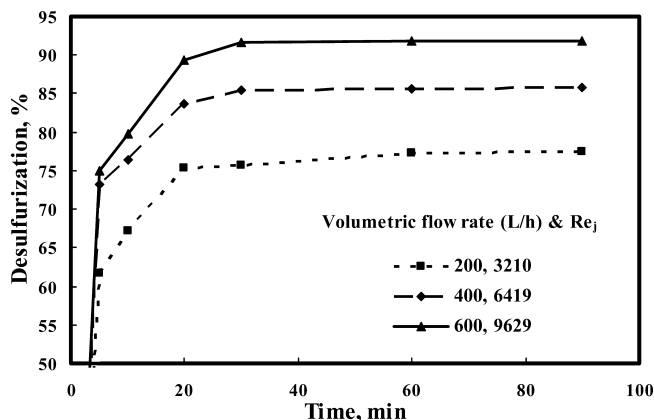
Figure 9. Effect of the volumetric flow rate and Re_j on the performance of FIJR. FIJR conditions: jet diameter = 3 mm; internozzle distance = 1 cm. Oxidation conditions: hydrogen peroxide−formic acid system; initial total sulfur content of kerosene = 2335 ppmw; O/S molar ratio = 5; acid/S molar ratio = 30 (i.e., 207 mL of H_2O_2 and 459 mL pf formic acid were used for oxidation of 7.0 L of kerosene). Extraction conditions: T = 25 °C; solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

with an increase in the number of jets. However, the power input requirement increases as well. Therefore, the optimum number of jets should be determined by economical considerations.

There are a number of flow and geometric parameters such as the volumetric flow rate, jet diameter, and the internozzle distance in the impinging-jets reactor affecting the performance of the reactor. The range of these specific parameters in the present study was selected according to our previous experiences in the design and operation of this kind of reactors.[49,55] In the present study, the selected range of the jet diameter was 2−4 mm, which is the same as that used in our previous study.[49,55] Since in the present reactor (i.e., FIJR), the flow is distributed through four jets instead of two jets, a wider range of the volumetric flow rate (i.e., 200−600 L/h) was selected compared to our previous work.[49,55] The selected range of internozzle distance was 1−3 cm, which is within the selected range used for this parameter in the previous study.[55] According to our experiences, the effects of the above-mentioned parameters outside of the selected ranges are minor.

In what follows, the influences of main operating and design parameters of FIJR on the ODS of kerosene have been presented as well as the comparison of performance capability of FIJR with that of STR.

3.2.1. Effect of Feed Flow Rate. Figure 9 shows the variation of desulfurization versus time with the volumetric flow rate of feed as a parameter at a jet diameter of 3 mm. As can be observed, an increase in the jet Reynolds number (Re_j) results in an increase in the desulfurization. This can be attributed to the reduction of the mass-transfer resistance between two aqueous and organic phases as a result of increasing in the turbulence in the reaction chamber of the reactor. Dehkordi[54] reported an increase in the overall volumetric mass transfer coefficients of liquid−liquid systems in impinging-jets contactors. It should be added that quantitative evaluation of mass transfer coefficients in the present system is a difficult task due to complexity of the system and unknown reaction rates. For the system under consideration, the jet velocity exiting from the tip of the nozzles was calculated to be 1.96, 3.93, and 5.89 m/s for the feed flow rates of 200, 400, and 600 L/h, respectively.

3.2.2. Effect of Jet Diameter. To investigate the effect of the jet diameter on the desulfurization performance, a number of experiments were carried out with the jet diameter ranging
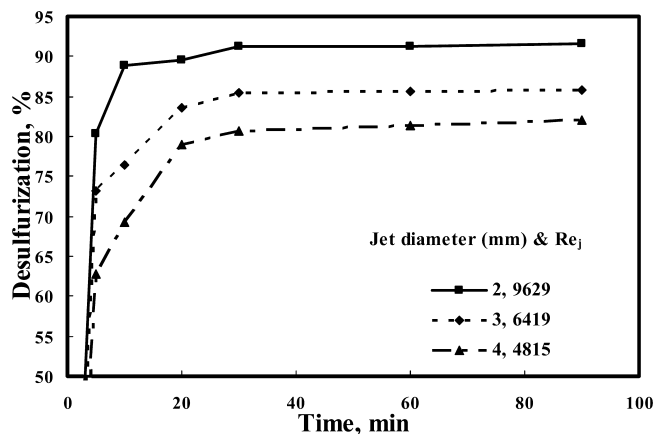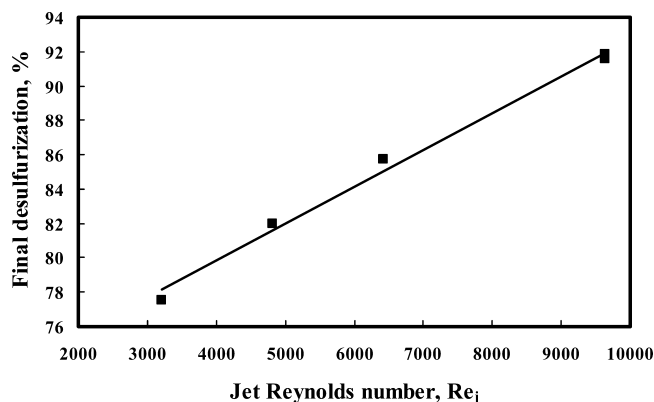
Figure 10. Effect of the jet diameter and Re_j on the performance of FIJR. FIJR conditions: feed flow rate = 400 L/h; internozzel distance = 1 cm. Oxidation conditions: hydrogen peroxide−formic acid system; initial total sulfur content of kerosene = 2335 ppmw; O/S molar ratio = 5; acid/S molar ratio = 30 (i.e., 207 mL of H_2O_2 and 459 mL of formic acid were used for oxidation of 7.0 L of kerosene). Extraction conditions: T = 25 °C; solvent. acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

Figure 11. Effect of Re_j on the final desulfurization of FIJR. FIJR conditions: Internozzel distance = 1 cm. Oxidation conditions: hydrogen peroxide−formic acid system; initial total sulfur content of kerosene = 2335 ppmw; O/S molar ratio = 5; acid/S molar ratio = 30 (i.e., 207 mL of H_2O_2 and 459 mL of formic acid were used for oxidation of 7.0 L of kerosene). Extraction conditions: T = 25 °C; solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

from 2 to 4 mm and at constant volumetric feed flow rate of 400 L/h. The experimental results are shown in Figure 10. A decrease in jet diameter from 4 to 2 mm increases the jet Reynolds number from 4815 to 9629 and increases the desulfurization performance. This is due to bulk turbulence produced by eddies in the reaction chamber. Figure 11 shows variations of the final desulfurization versus jet Reynolds number. As can be observed, there is a direct relationship between the final desulfurization and jet Reynolds number. It is important to note that the same desulfurization is obtained at jet Reynolds number of 9629 for two different operating conditions (i.e., (case 1) jet diameter = 3 mm and feed volumetric flow rate = 600 L/h; and (case 2) jet diameter = 2 mm and feed volumetric flow rate = 400 L/h). The calculated power input for cases 1 and 2 are 8.33 and 5.55 W, respectively. Thus, case 2 is superior to case 1 due to the lower power input requirement for the same desulfurization. To determine the power inputs, during the experiments, the pressure drop across FIJR was measured. The total power input requirement (P_t) was determined as follows:

$$P_t = Q\Delta P \tag{1}$$

where Q and ΔP are feed volumetric flow rate and the pressure drop across FIJR, respectively.

3.2.3. Effect of Internozzle Distance. To examine the effect of the jet internozzle distance on the desulfurization, a number of experiments at a constant volumetric flow rate of 400 L/h, and the jet diameter of 3 mm with different internozzle distances ranging from 1−3 cm were carried out. The experimental results are shown in Figure 12. As can be observed, a decrease in the internozzle distance results in an increase in the desulfurization due to an increase in the turbulence in the reaction chamber, which leads to a decrease in mass-transfer resistance.

3.3. Evaluation of Performance Capability of FIJR. To compare the performance capability of FIJR for the ODS of kerosene with conventional reactor systems such as STR, a number of experiments with the identical O/S, acid/S, operating temperature, reaction time, and the same power input requirement were carried out. Figure 13 shows the desulfurization performances for two reactor types (i.e., FIJR and STR). Considering the operating conditions of STR (i.e., ΔP = 0.1 bar and Q = 100 L/h) and applying eq 1, the power input requirement for the pump in the STR is 0.28 W. To obtain the same power input requirement for FIJR and STR, the power input requirement for the impeller should be (5.55 − 0.28 = 5.27 W) because the total power input of FIJR is 5.55 W. Regarding the flat six-blade turbine impeller with four baffles in the tank, the power number (N_P) obtained from the relevant curve[69] is 6.5 for Re > 10000. Using this value of N_P and physical properties of reaction mixture, the rotation speed of the impeller (N) can be calculated by eq 2 as follows:

$$N_P = \frac{P_i}{(\rho N^3 D^5)} \tag{2}$$

where P_i, ρ, N, and D are power input by impeller (W), fluid density (kg/m³), impeller speed (cycle/s), and impeller diameter (m), respectively. N_P for the impeller used in the present work (i.e., flat six-blade turbine impeller with four baffles in the tank) and for Re > 10000 is about 6.5. Therefore, considering ρ = 990.5 kg/m³ (mixture density), D (impeller diameter) = 4.5 cm, we get N = 986 rpm.

Figure 13 demonstrates the performance of FIJR and STR at the same power input. As can be observed from this figure, the performance of FIJR is superior, which can be attributed to complex flow pattern within the reaction chamber, and strong collision of the jets within the reaction chamber especially at the impingement zone leading to a decrease in mass transfer resistances. Note that the performance of FIJR and STR are compared under the same design and operating conditions such as contact time.

4. Conclusions

An experimental investigation was conducted on the ODS of nonhydrotreated kerosene as a typical light fuel oil with an initial sulfur content of 2335 ppmw using oxidation with hydrogen peroxide−formic acid oxidation system followed by liquid−liquid extraction. The influences of various operating conditions such as the reaction temperature, O/S molar ratio, and the acid/S molar ratio on the performance of the ODS process were carefully examined and the appropriate values of each operating condition were found. A novel type of four-impinging-jets reactor (FIJR) was proposed and successfully tested as a chemical reactor for the desulfurization of nonhy-
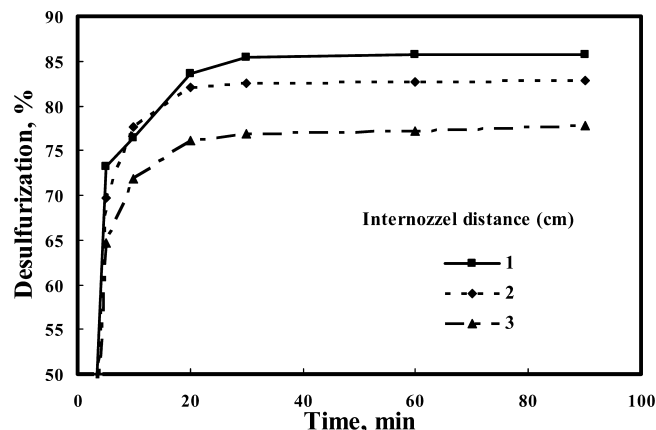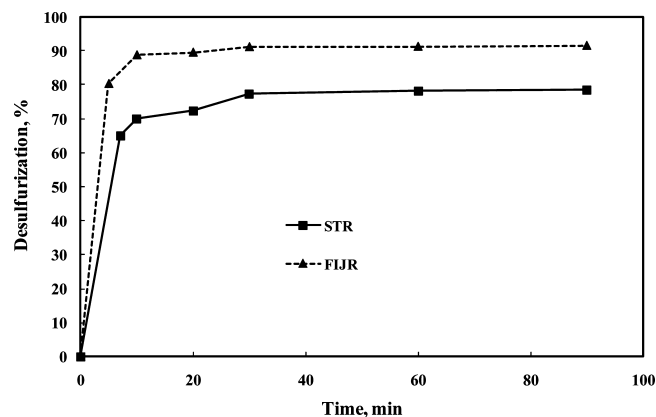
Figure 12. Effect of jet internozzle distance on the performance of FIJR. FIJR conditions: feed flow rate = 400 L/h; jet diameter = 3 mm. Oxidation conditions: hydrogen peroxide—formic acid system; initial total sulfur content of kerosene = 2335 ppmw; O/S molar ratio = 5; acid/S molar ratio = 30 (i.e., 207 mL of H_2O_2 and 459 mL of formic acid were used for oxidation of 7.0 L of kerosene). Extraction conditions: $T = 25$ °C; solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

Figure 13. Desulfurization vs time for different types of reactor. Oxidation conditions: hydrogen peroxide—formic acid system; initial total sulfur content of kerosene = 2335 ppmw; O/S molar ratio = 5; acid/S molar ratio = 30 (i.e., 207 mL of H_2O_2 and 459 mL of formic acid were used for oxidation of 7.0 L of kerosene). Extraction conditions: $T = 25$ °C; solvent, acetonitrile with (S/F) = 0.5; no. of extraction stages = 2.

drotreated kerosene via oxidation process. The influences of various operating and design parameters such as the jet Reynolds number, feed flow rate, internozzle distance, and the jet diameter on the performance capability of FIJR were successfully investigated and about 92% desulfurization was obtained. The performance capability of FIJR was also compared to a conventional stirred-tank reactor (STR). The results obtained in the FIJR clearly indicate that FIJR has a better performance for the ODS process and is a promising contacting device.

Acknowledgment

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