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PROCESS MODELING AND KINETIC ESTIMATION FOR DESULFURIZATION OF DIESEL FUEL USING NANO - ZnO/Al_2O_3

Article Highlights

- Nano ZnO/γ-Al_2O_3 was synthesized, characterized, and used for the desulfurization of diesel fuel
- The process was conducted in a batch reactor at 30 to 90 °C and 20 to 80 min
- Sulfur removal was 93.781% using 9% ZnO/γ-Al_2O_3 at 90°C and 80 min
- Process modeling and kinetic estimation for desulfurization were investigated
- Simulation results indicate less than 5% error between experimental and predicted results

Abstract

In the present paper, a gamma alumina (γ-Al_2O_3) loaded zinc oxide (ZnO) nano-catalyst (ZnO/γ-Al_2O_3) has been synthesized and used to accelerate the removal of sulfur compounds from light gas oil by oxidative desulfurization (ODS) process. The synthesized nano-catalysts have been characterized by atomic force microscopy (AFM) and Brunauer-Emmett-Teller (BET). The ODS process has been conducted in a batch reactor at various reaction temperatures and batch times varying between 30 to 90 °C and 20 to 80 min, respectively. DBT removal was highest (93.781%) while using synthesized nano-catalyst (9% ZnO/γ-Al_2O_3) at 90°C and 80 min reaction time. Based on the obtained experimental data, a new mathematical modeling technique was performed for the ODS operation under mild experimental conditions to evaluate the most appropriate kinetic variables for the newly synthesized nano-catalysts. Simulation results indicate a good match with experimental observations with less than 5% absolute average error for all runs. The optimization procedure of the process condition displays that > 98% DBT could be eliminated within 200 min, at 87 °C, in the existence of synthesized nano-catalyst (9% ZnO/γ-Al_2O_3).

Keywords: gamma alumina; model; nano-catalyst; optimization; sulfur; zinc oxide.

Recently, the produced hydrocarbon feedstock has contained a high amount of sulfur compounds, negatively influencing the refining operations and the quality of the resulting fuels. Sulfur oxides (SO_2) emitted while burning fuels have an adverse effect on human health and the environment and lead to acid rain and corrosion [1–3]. In this regard, strict environmental regulations have been applied in many countries limiting the sulfur concentration in light fuels to 10 ppm. Since the rise in sulfur compounds level in oils causes an increase in the hydrodesulfurization (HDS) cost, the concern of researchers has been growingly attracted by non-hydrogen desulfurization techniques [4,5]. Oxidative desulfurization (ODS) is the most advantageous and promising technique among the non - hydrogen desulfurization techniques (bio

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desulfurization, adsorption, extraction) [5–7]. The major features of ODS are lower pressures and temperatures and the absence of hydrogen [8,9]. Another feature of ODS is the ability to eliminate organic sulfur compounds not cracked in the process of HDS [5]. Organic sulfur compounds are treated with an oxidizing agent and a catalyst to oxidize first to their corresponding sulfoxides and then to their sulfones, which are more polar compounds, and then these oxidized sulfur compounds are separated from the fuel by employing an extraction technique with a polar extractant such as dimethyl formamide, acetonitrile, methanol, etc. or by utilizing adsorption technique [10]. Mathematical modeling is the description of a system by employing mathematical equations. It is significant to capture the fundamental characteristics of a system to design (describe), predict (forecast), optimize the operating conditions, and design an appropriate controller. Some utilizing areas of mathematical modeling are operation control, process design, operations training simulators, process safety, environmental effect assessment, etc. Each field of application may need various systems of mathematical model equations. Mathematical modeling includes analysis, numerical simulation, and experimental tests [11]. The optimization process is utilized in several fields to determine solutions of studies that minimize or maximize some interesting parameters, like maximizing profits, lowering costs in the production of a good or service, enhancing production, or reducing raw materials [12]. Nanostructures (size of particle less than 100 nm) have been recently utilized in catalytic processes. Nano-catalysts applied in this technique are environmentally friendly, lower cost, and have good mechanical strength. Also, nanostructured materials have significant porosity, purities, chemical and thermal stability, and density tunable. In addition, nano-catalysts have significant recyclability in the oxidative desulfurization technology [13]. Developing a new nanocatalyst with remarkable properties that enhances its activity towards the high efficiency of the ODS process for fuel is an interesting goal in the industrial and academic fields. Also, finding a mathematical model that evaluates the optimal kinetic variables of the oxidation process in the presence of the newly synthesized nano-catalysts is the main matter in improving, designing, and scaling up the ODS for the industrial fields. Two reported works in the literature studied oxidative desulfurization of fuel in the presence of heterogeneous catalysts composed of gamma-alumina (γ-Al_2O_3) as support and ZnO as active metal. Nawaf *et al.* [14] investigated the removal of sulfur compounds in kerosene by employing (18% ZnO / γ-Al_2O_3) as a catalyst and air as an oxidizing agent in a batch reactor. It was found that 70.5% of sulfur compounds were removed under a reaction time of 50 min and a reaction temperature of 190 °C. Abdulateef *et al.* [15] investigated the oxidative desulfurizing experimentally by utilizing (12.5% ZnO-12.5% MgO)/γ-Al_2O_3 as a catalyst, where sulfur conversion of 84.6% was achieved under reaction time of 45 min and reaction temperature of 190°C employing a batch mode reaction.

In this study, a new mathematical model has been built, validated, and optimized for ODS technology to evaluate the optimal kinetic variables in the presence of the newly synthesized nano-catalysts based on the obtained results of the oxidation experiments at mild operating conditions. Finally, the evaluated kinetic parameters will be utilized to estimate the optimal ODS operating condition, maximize the sweetening of diesel fuel, and produce cleaner fuel.

MATERIALS AND METHODS

Diesel fuel produced by OMV Company (Pendik-Istanbul-Turkey) was utilized as a feedstock in the ODS process with an Initial sulfur concentration of 9 ppm. Dibenzothiophene (DBT) supplied by (Sigma Aldrich) was employed as the model refractory aromatic sulfur compounds (purity of ~98%). Nanoparticles of gamma alumina (obtained from Sky Spring Nanomaterials Inc.) were utilized as catalyst support< the γ-Al_2O_3 properties are illustrated in Table 1.

Table 1. Properties of γ-Alumina nanoparticle.

Properties	Values	Unit
Bulk density	0.333	g/m^3
BET surface area	500.0	m^2/g
Pore volume	1.50	cm^3/g
Pore size	20	nm

Zinc acetate {$Zn(CH_3COO)_2.2H_2O$)} obtained from (Sigma) has been employed as the active metal in the prepared nano-catalyst with a purity of 99%. Hydrogen peroxide (H_2O_2), provided by Aldrich Company with a purity of 99.99%, has been used in the ODS reaction as a source of oxygen atoms that oxidize the sulfur compounds to sulfoxides and sulfones. Zinc oxide (ZnO) was loaded on γ-Al_2O_3 with 3%, 6%, and 9% (weight %) via an incipient wetness impregnation (IWI). At first, γ-Al_2O_3 was introduced in deionized water with stirring for half an hour. After that, $Zn(CH_3COO)_2{\cdot}2H_2O$) was mixed with the dispersed γ-Al_2O_3 support with stirring for 5 h under 95 °C. The resultant material was dried under 95 °C in an oven overnight and finally calcined for 3 h at 300 °C by using a furnace with a temperature ramping rate of 3 °C/min to produce nano-

catalysts (ZnO/ γ-Al_2O_3) with various loading of ZnO. The oxidative desulfurization process was applied in a batch reactor by employing hydrogen peroxide (H_2O_2) as an oxidizing agent and diesel fuel as feedstock with an initial sulfur (DBT) concentration of 611 ppm. The oxidation reaction was conducted at various process conditions (reaction temperature and operating time) to evaluate the ODS reaction efficiency in the presence of the synthesized nano-catalyst. The ODS technology is presented in Figure 1.

The mathematical modeling technique for the ODS process was applied by the software of gPROMS (General Process Modeling System) [13]. The group of equations employed in the mathematical modeling technique for ODS operations is summarized in Table 2.

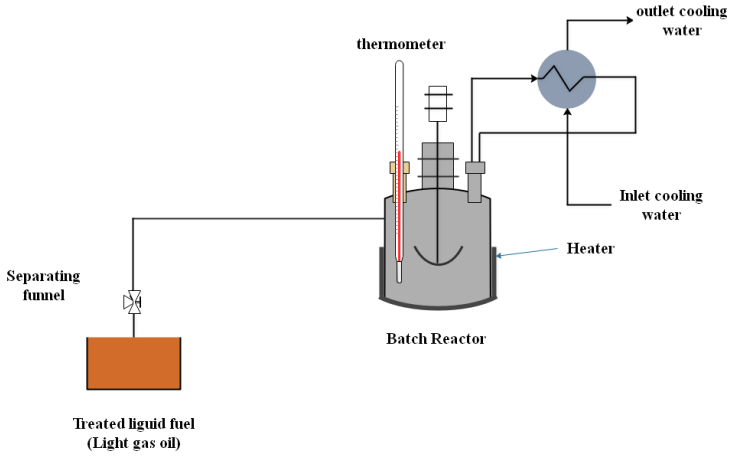

Figure 1. Schematic diagram of the ODS process.

Table 2. Equations employed in the Mathematical modeling technique.

Parameter	Equations/values	Eq.	Reference
Reaction rate ($-r_{DBT}$)	$(-r_{DBT}) = \eta_0 \, A \, {C_{DBT}}^n$	(1)	[16]
Arrhenius equation (A)	$A=A_0 e^{(-\frac{EA}{RT})}$	(2)	[17,18]
The final sulfur concentration (C_{DBT})	$C_{DBT} = [\, {C_{DBT,t}}^{(1-n)} + (n-1).t.A_{in}\,\eta_0]^{(\frac{1}{1-n})}$	(3)	[19]
The effectiveness factor (η_0)	$\eta_0 = \frac{3(\phi \coth\phi - 1)}{\phi^2}$	(4)	[19,20]
Thiele modulus (ϕ)	$\phi = \frac{V_P}{S_P}\sqrt{(\frac{n+1}{2})\frac{A_{in}\,{C_{DBT}}^{(1-n)}\rho_p}{D_{ei}}}$	(5)	[19,20]
Effective diffusivity (D_{ei})	$D_{ei} = \frac{\varepsilon_B}{\mathcal{T}}\frac{1}{\frac{1}{D_{mi}}+\frac{1}{D_{ki}}}$	(6)	[16,20]
Porosity (ε_B)	$\varepsilon_B = V_g\rho_p$	(7)	[16,20]
Particle density (ρ_p)	$\rho_p = \frac{\rho_B}{1-\varepsilon_B}$	(8)	[16,20]
The tortuosity factor ($\mathcal{T}$)	The tortuosity factor value ($\mathcal{T}$) of the pore network ranged between (2.0 to 7.0)	----	[20]
The Knudsen diffusivity (D_{ki})	$D_{ki} = 9700\, r_g(\frac{T}{Mw_{DBT}})^{0.5}$	(9)	[16,19]
Mean pore radius (r_g)	$r_g = 2V_g/S_g$	(10)	[21]
The molecular diffusivity (D_{mi})	$D_{mi} = 8.93 * 10^{-8}(\frac{{v_{DF}}^{0.267}T}{{v_{DBT}}^{0.433}\mu_{DF}})$	(11)	[22,23]
DBT molar volume (v_{DBT})	$v_{DBT} = 0.285(v_{CDBT})^{1.048}$	(12)	[22]
Diesel fuel molar volume (v_{LGO})	$v_{DF} = 0.285(v_{cDF})^{1.048}$	(13)	[20]
Critical volume of diesel fuel (v_{cLGO})	$v_{cDF} = (7.5214 * 10^{-3}(T_{meABP})^{0.2896}(\rho_{DF,15.6})^{-0.7666})Mw_{DF}$	(14)	[20]
The catalyst's external volume (Vp) (sphere particle)	$V_p = \frac{\pi}{6}(d_p)^3$	(15)	[23]
The catalyst's external surface (Sp) (sphere particle)	$S_p = \pi(d_p)^2$	(16)	[23]
Viscosity of fuel (μ_{LGO})	$\mu_{LGO} = 3.141 * 10^{10}(T-460.0)^{-3.444}(logAPI)^{\alpha}$	(17)	[24]
Dimensionless No. (α)	$\alpha = 10.3130[log_{10}(T-460)] - 36.4470$	(18)	[24]
American petroleum institute (API)	$\text{API} = \frac{141.50}{sp.gr_{DF15.6}} - 131.50$	(19)	[25]

The most accurate values of kinetic parameters can be determined by minimizing the difference between the results of practical experiments and the estimated results by applying the model. To estimate the accurate parameters values of the kinetic model, the minimization of the following objective function was:

$$OBJ = \sum_{n=1}^{N_t} \left(C_{DBT}^{\exp} - C_{DBT}^{pred} \right)^2 \quad (1)$$

where Nt is the experimental runs number, C_{DBT}^{exp} is the experimental results, and C_{DBT}^{pred} is the predicted modeling results.

The amount of DBT removal can be estimated based on the following equation:

$$X_{DBT} = 1 - \frac{C_{DBT}}{C_{DBT_t}} \quad (2)$$

where, X_{DBT} is the conversion of the DBT compound.

An optimization problem has been formulated for the evaluation of the kinetic model parameter to obtain the order of reaction (n), the pre-exponential factor (*A*o), and activation energy (EA) for each prepared catalyst by minimizing the sum of squared error (SSE) by subjecting the constraints of operation under given ODS conditions. The estimation of kinetic parameters is formulated as described in Table 3.

Table 3. Formulation of optimization problem of parameter estimation.

Given	Obtain	So as to minimize	Subjected to
Synthesized nanocatalyst Reactor formation ODS conditions	Order of reaction (n), the pre-exponential factor (Ao), and activation energy (EA) for each prepared catalyst.	Sum of squared error (SSE).	Constraints of operation

RESULTS AND DISCUSSION

Characterization of (ZnO/ γ-Al_2O_3) nano-catalyst

The BET test was achieved to reveal the pore dimensions and BET surface area of the synthesized nano-catalyst. As illustrated in Table 4, the results of BET detected that after zinc oxide (ZnO) loading, the volume of pores and the specific surface area reduce remarkably while the pore size rises. This behavior is attributed to the occupancy of zinc oxide in some spaces within the samples [13]. So, improving the performance of oxidative desulfurization reactions employing (ZnO/γ-Al2O3), nano-catalyst can be returned to enhance the catalyst properties and activity via ZnO loading.

The average particle size distribution of synthesized (ZnO/ γ-Al_2O_3) nano-catalysts was estimated by utilizing the AFM test. As shown in Figure S1 (Supporting material), the average particle size for all synthesized nano-catalysts is less than 100 nm, where the average nanoparticle diameter (d_p) is 79.05 nm for 3% ZnO/ γ-Al_2O_3, 81.35 nm for 6% ZnO/ γ-Al_2O_3 and 84.54 nm for 9% ZnO/ γ-Al_2O_3.

Table 4. BET results of synthesized (ZnO/ γ-Al_2O_3) nano-catalysts.

Sample	Pore volume (cm^3/gm)	Specific surface area (m^2/gm)	Pore size (nm)
γ-Al_2O_3	1.5	500	20
3% ZnO/ γ-Al_2O_3	0.6342	457.462	27.183
6% ZnO/ γ-Al_2O_3	0.2954	413.218	33.149
9% ZnO/ γ-Al_2O_3	0.0846	388.765	39.543

Oxidative desulfurization results

The effect of ZnO loaded over the catalyst support on the removal of DBT compounds was evaluated by loading various amounts of ZnO (3%, 6%, and 9%) over the support of the catalyst. Figure 2 displays the impact of ZnO loading on the ODS efficiency. The removal of DBT compounds was enhanced by raising the loading ZnO over the catalyst's support. It might be owing to the availability of active sites that promote the activity of the ODS reaction. Also, the performance of the ODS process is remarkably improved via upgrading the catalyst properties and activity after ZnO loading.

The influence of temperature on the efficiency of the ODS reaction was investigated, and the results are presented in Figure 3.

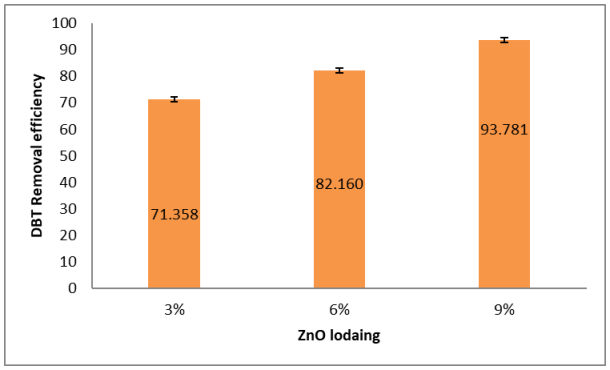

Figure 2. The effect of ZnO loading on the DBT elimination efficiency in ODS reaction.

For all synthesized nano-catalysts, the results detected that the removal of DBT accelerated with a rising reaction temperature. An increase in the reaction temperature enhances the movement of the molecules, which enhances the chance of collision and reaction between sulfur compounds and the oxidant. Also, at higher temperatures, the most robustly adsorbed sulfones will be eliminated from the catalyst surface readily [26–30]. The enhancement in the oxidation reactions can also be returned to improve the mass and heat transfer rates between the reacting species by enhancing the oxidation temperature. The increase in oxidation temperature can impact the physical properties of the fuel, like the density and viscosity, by reducing it, which leads to a high mass transfer rate and significantly faster oxidation reaction [1,2].

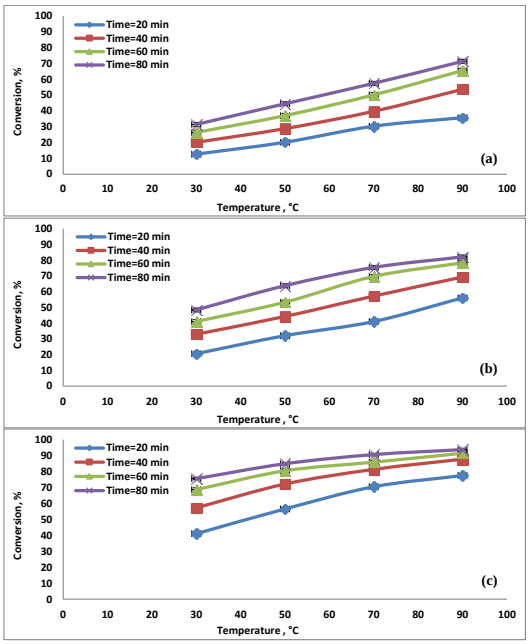

Figure 3. The effect of reaction temperature on the efficiency of ODS reaction for (a) 3% ZnO/ γ-Al_2O_3 (b) 6% ZnO/ γ-Al_2O_3 (c) 9% ZnO/ γ-Al_2O_3.

The reaction times effect on the removal of DBT compounds is illustrated in Figure 4. The DBT removal was promoted with increasing reaction time due to the enhanced reaction chance between DBT compounds and oxidizing agents with increasing reaction times. Also, the increasing collision time improved the mass transfer between the reacting materials and gave more time for catalyst activity through the reacting media, which led to high removal efficiency for sulfur compounds from the fuel [1,3].

Kinetic parameters estimation

The constant parameters utilized in the mathematical model are listed in Table 5. The optimal kinetic parameter values determined via the mathematical modeling are summarized in Tables S1–S3 next.

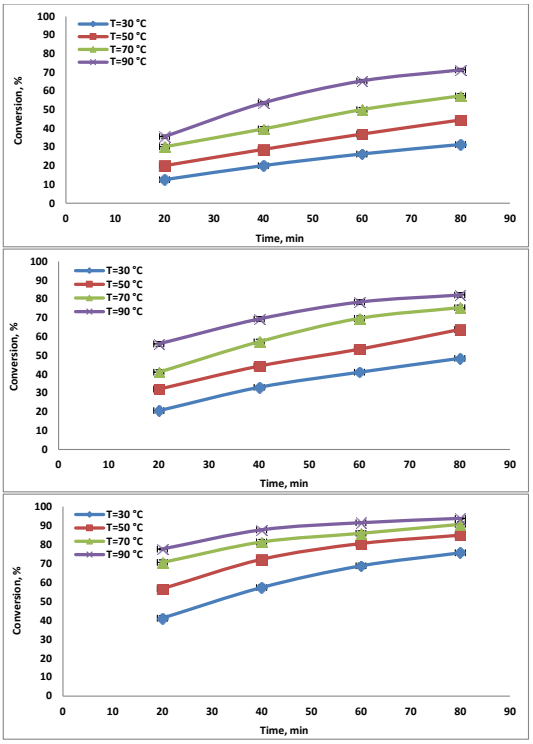

Figure 4. The effect of reaction time on the efficiency of ODS reaction for (a) 3% ZnO/ γ-Al_2O_3 (b) 6% ZnO/ γ-Al_2O_3 (c) 9% ZnO/ γ-Al_2O_3.

According to the data illustrated in these Tables, it is concluded that the (9% ZnO/ γ-Al_2O_3) nano-catalyst is superior to the other catalysts based on the reaction order at similar operation conditions. The reaction order of the (9% ZnO/ γ-Al_2O_3) is less than other catalysts, which denotes that the reaction rate in existence (9% ZnO/ γ-Al_2O_3) is faster than the other synthesized nano-catalysts.

Experimental and simulation data

The simulation of ODS technology is conducted by employing the gPROMS software. The experimental data and expected simulation are summarized in Tables S4 to S6.

Optimal operation conditions for a minimum DBTconcentration

The best values of process conditions are estimated using the most accurate values of kinetic parameters attained by applying the simulation process. Predicting the best operating conditions values for achieving the minimum sulfur content is essential. Therefore, the optimization technique is built as follows:

Given: Interaction order, reactor performance, catalyst, and k_o and EA for the interaction.

Obtain: The better operating conditions for high

Table 5. Constant parameters employed in the mathematical modeling technique.

Parameter, unit	Value
Initial concentration of DBT compounds ($C_{DBT.t}$), ppm	611
Time, min	$time_1$=20, $time_2$=40, $time_3$=60, $time_4$=80
Temperature (T), °C	T_1 = 30, T_2 = 50, T_3 = 70, T_4 = 90
Diesel fuel density at 15.5°C (ρ_{DF}), gm/cm^3	0.8205
Mean average boiling point (T_{meABP}), °R	957
Acceleration gravity (g), m/sec^2	9.81
Gas constant (R), J/mole.°K	8.314
Pore volume per unit mass of catalyst (Vg), cm^3/gm	Vg, (3% ZnO/ γ-Al_2O_3) = 0.6342 Vg, (6% ZnO/ γ-Al_2O_3) = 0.2954 Vg, (9% ZnO/ γ-Al_2O_3) = 0.0846
Specific surface area of a particle (Sg), cm^2/gm	Sg, (3% ZnO/ γ-Al_2O_3) = 4574620 Sg, (6% ZnO/ γ-Al_2O_3) = 4132180 Sg, (9% ZnO/ γ-Al_2O_3) = 3887650
Catalyst particle volume (Vp), cm^3	Vp, (3% ZnO/ γ-Al_2O_3) = 3.163*10^{-16} Vp, (6% ZnO/ γ-Al_2O_3) = 2.818*10^{-16} Vp, (9% ZnO/ γ-Al_2O_3) = 3.163*10^{-16}
External surface area of a particle (Sp), cm^2	Sp, (3% ZnO/ γ-Al_2O_3) = 1.963*10^{-10} Sp, (6% ZnO/ γ-Al_2O_3) = 2.079*10^{-10} Sp, (9% ZnO/ γ-Al_2O_3) = 2.245*10^{-10}
Bulk density (ρ_B), gm/cm^3	$\rho_{B.}$ (3% ZnO/ γ-Al_2O_3) =0.343 $\rho_{B.}$ (6% ZnO/ γ-Al_2O_3) =0.351 $\rho_{B.}$ (9% ZnO/ γ-Al_2O_3) =0.386
Diesel fuel molecular weight (M_{wLDF}), gm/mole	200.468
Sulfur molecular weight (M_{wDDT}), gm/mole	32.06
Mean pore radius (r_g), nm	r_g, (3% ZnO/ γ-Al_2O_3) =2.772 r_g, (6% ZnO/ γ-Al_2O_3) =1.429 r_g, (3% ZnO/ γ-Al_2O_3) =0.352

removal of sulfur.

So as to minimize: Sulfur content.

Subjected to: Constraints in the operation.

The problem is formulated mathematically as follows:

$$Min \quad C_{DBT}$$

$$T^j, time_i^j, C_{DBT}^j \quad \begin{pmatrix} j = 3\% ZnO / \gamma - Al_2O_3, \\ 6\% ZnO / \gamma - Al_2O_3 \ \& \\ 9\% ZnO / \gamma - Al_2O_3 \end{pmatrix}$$

$$S.t.f\left(z, x(z), \dot{x}(z), u(z), v\right) = 0 \quad time_L^j \le time^j \le time_U^j$$

$$C_{DBT.tL}^j \le C_{DBT.t}^j \le C_{DBT.tU}^j$$

$$T_L^j \le T^j \le T_U^j$$

$$X_{DBT.tL}^j \le X_{DBT.t}^j \le X_{DBT.tU}^j$$

The optimization solution method is conducted by applying the gPROMS program. The optimal operating conditions for each synthesized nano-catalysts are illustrated in Tables S7 to S9.

CONCLUSION

The desulfurization of DBT via oxidation technology in diesel fuel fraction was conducted in a batch reactor at various operating conditions (reaction temperatures and reaction times), utilizing a synthesized nano-catalyst (ZnO/γ-Al_2O_3) and oxidant of hydrogen peroxide as oxidant, at (1 atm) to reach the minimum DBT content. The ODS system in this paper is highly effective in eliminating DBT compounds found in the light gas oil cut, where the maximum DBT removal of (93.8%) was achieved under a temperature of 90 °C in 80 min in the presence of a synthesized nano-catalyst (9% ZnO/γ-Al_2O_3). Also, the high quality of light gas oil fuel was achieved by minimizing the sulfur concentration by applying mathematical modeling technology. The optimal values of operating conditions to obtain cleaner fuel (DBT elimination > 98%) were a processing time of 200 min and a process temperature of 87 °C with the synthesized nano-catalyst (9% ZnO/γ-Al_2O_3). The new mathematical model for the ODS reactions is evaluated as the most appropriate kinetic variable for the newly synthesized nano-catalysts under mild operating conditions. Also, finding a mathematical model is the main matter in improving, designing, and scaling up the ODS for the industrial fields.

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NAUČNI RAD

MODELOVANJE I KINETIČKA PROCENA PROCESA DESUMPURIZACIJE DIZEL GORIVA KORIŠĆENJEM NANO- ZnO/Al_2O_3

U ovom radu, sintetisan je nano-katalizator sa cink-oksidom (ZnO) nanetim na γ-alumini (γ-Al_2O_3), tj. ZnO/g-Al_2O_3, namenjen ubrzavanje uklanjanja jedinjenja sumpora iz lakog gasnog ulja oksidativnom desulfurizacijom. Sintetizovani nanokatalizatori su okarakterisani mikroskopijom atomskih sila i Brunauer-Emet-Telerove metode. Oksidativna desulfurizacija je sproveden u šaržnom reaktoru na različitim temperaturama i vremenima reakcije (30–90 °C i 20–80 min). Uklanjanje dibenzotiofena je bilo najveće (93,8%) pri korišćenju sintetizovanog nanokatalizatora (9% ZnO/ γ-Al_2O_3) na 90 °C za 80 min. Na osnovu dobijenih eksperimentalnih podataka, izvedena je nova tehnika matematičkog modelovanja oksidativne desulfurizacije u blagim eksperimentalnim uslovima kako bi se procenile najprikladnije kinetičke promenljive za novosintetizovane nanokatalizatore. Rezultati simulacije ukazuju na dobro poklapanje sa eksperimentalnim zapažanjima sa manje od 5% apsolutne prosečne greške za sve serije. Procedura optimizacije uslova procesa sa nanokatalizatora (9% ZnO/ γ-Al_2O_3) pokazuje da se više od 98% dibenzotiofena može eliminisati u roku od 200 min, na 87 °C.

Ključne reči: γ-alumina; model; nano-katalizator; optimizacija; sumpor; cink oksid.