

Experimentation, Modelling and Optimisation of Oxidative Desulphurization of Heavy Gas Oil: Energy Consumption and Recovery Issues

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Deep desulphurization of a model sulfur compound dibenzothiophene (DBT) and heavy gas oil (HGO) is studied with hydrogen peroxide (H_2O_2) as oxidant and formic acid (HCOOH) as catalyst using a lab-scale batch reactor. The results are quite promising and therefore a large scale oxidation process using a continuous stirrer tank reactor (CSTR) is considered further. Large amount of energy is required to carry out reaction at temperature same as the batch reactor, the recovery of which is very important for maximizing the profitability of operation and reducing environmental impact. Therefore we have proposed a heat integrated CSTR system. In the absence of a real plant we have developed a process model for the system. The kinetic model for the CSTR is based on the batch reactor experiments. An optimization problem to minimize the overall annual plant cost is formulated and solved using gPROMS. A cost saving of 36% for the integrated process is obtained compared to a non-integrated process.

1. Introduction

The removal of sulfur from petroleum or its products is necessary for both industrial and environmental reasons. Sulfur in petroleum products poisons catalytic converters, corrodes parts of internal combustion engines and refineries because of the formation of oxy-acids of sulfur. The conventional method for reducing sulfur is catalytic hydrodesulfurization (HDS), which requires high partial pressure of hydrogen and high temperature, making HDS a costly option for deep desulfurization. Furthermore HDS is not effective for removing hetrocyclic sulfur compounds such as dibenzothiophene (DBT) and its derivatives. Faced with continuing fuel quality challenges, refiners have begun to look at oxidative desulfurization (ODS), under much milder conditions, as an alternative complementary process to HDS for deep desulfurization (Aida et. al., 2000). The ODS is basically a two-stage process, oxidation, followed by liquid extraction. In the oxidation step, the sulfur containing compounds are oxidized using appropriate oxidants to convert these compounds to their corresponding sulphones. These are preferentially extracted from oil based on their increased relative polarity (Babich and Moulijn, 2003, Gore; 2001). In the extraction step, the oxidized compounds are extracted from the oil by using a non-miscible solvent.

Within this context, the aim of the present work is two fold. On the one hand we study the oxidation with H_2O_2 of model sulfur compound (DBT) and sulfur present in heavy gas oil (HGO) with a catalyst (HCOOH). A series of batch experiments are carried out

using a small reactor (500 ml) operating at various temperatures ranging from 40 °C to 100 °C. Kinetic model for the oxidation is also developed based on the experiments.

On the other hand, a CSTR model is developed for the oxidation process for evaluating viability of large-scale operation. It has been found that while the energy consumption and recovery issues could be ignored for batch experiments that are certainly not the case for large scale operation. Large amount of heating is necessary even to carry out the reaction even at 30-40 °C, the recovery of which is very important for maximizing profitability of operation. In industrial experience, the calculation of the minimum heating and cooling requirements reveal significant energy savings (Douglas, 1988). Here we proposed an integrated process where most of the energy is recovered. However, this leads to putting a number of heat exchangers in the system requiring capital investment. Therefore an optimization problem is formulated to minimise the total cost while optimizing several design and operating parameters such as reaction temperature, residence time, minimum approach temperatures and splitter ratio. The modelling and optimization are carried out by using gPROMS software (2005).

2. Small Scale Oxidation Process-Experiments using a Batch Reactor

In typical desulfurization reaction, dibenzothiophene (DBT) was dissolved in dodecane to a simulate model oil. The oxidation reaction was carried out in a 500 ml four necked flask containing 30 ml of model oil (sulfur was 940 ppm) and 1.25 ml of 30 % H₂O₂ (oxidant). The flask is placed into the heating mantel equipped with a temperature controller and stirred at 750 rpm. When the required reaction temperature has been reached 30 ml of HCOOH (catalyst) was added to the flask to initiate the reaction. This procedure was carried at different temperatures (40, 60, 80 and 100 °C) for different time intervals. The resulting mixture was cooled to room temperature, and the sulfur content of the organic layer was detected by X-ray fluorescence. The same procedure was used for the heavy gas oil (HGO, sulfur was 1066 ppm) using equal volumes of the catalyst and HGO (30 ml) and half the volume of oxidant (15 ml).

2.1 Experimental results

Figure 1 shows the results of oxidation of dibenzothiophene with H₂O₂ as a function of reaction time and reaction temperatures. The initial reaction rate increases with the increase in temperature. Ninety Eight (98) percent (wt%) conversion of DBT has been achieved after 5 minutes for all reaction temperatures. Figure 2 shows the oxidation of HGO with H₂O₂ as a function of reaction time over various temperatures. The results indicated that the oxidation activities increased with the increasing temperature up to 60°C but the conversion is only 40 %. A linear relationship of $\ln(C_A/C_{A0})$ versus time was obtained for DBT and total sulfur in HGO for all temperatures (Figures 3 and 4 shows the plot for 40 °C). These results suggest that the oxidative reaction can be treated as a first-order reaction. Therefore, the reaction rate constants at various temperatures can be obtained from the slopes of $\ln(C_A/C_{A0})$ vs time. The apparent activation energies (E) and Arrhenius factor (A) with model oil and HGO were obtained from the Arrhenius plots ($\ln k$ vs $1/T$). For HGO, E =7622 J/mol, A= 0.2279 min⁻¹ are obtained.

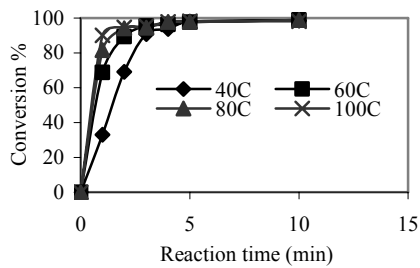


Fig.1. Oxidation of DBT at different reaction temperatures

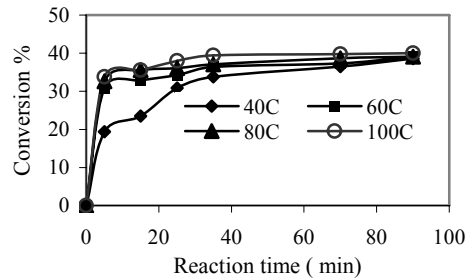


Fig.2. Oxidation of HGO at different reaction temperatures

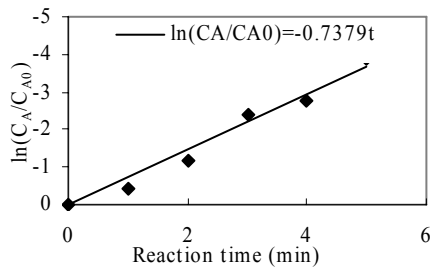


Fig.3. First-order plots DBT at 40 °C

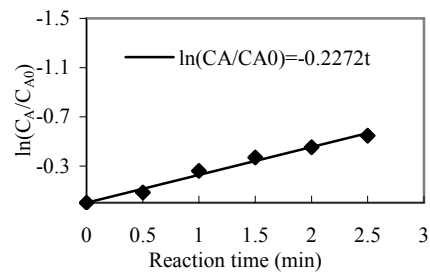


Fig.4. First-order plots of HGO at 40 °C

3. Large Scale Oxidation Process-Use of CSTR

We have chosen a CSTR for large scale oxidation. Batch reactor experiment shows that oxidation reaction of model sulfur compound and total sulfur in heavy gas oil is favourable at higher temperature ($>40^{\circ}\text{C}$). Energy consumption for batch reactor (lab-scale) was negligible and natural cooling after the reaction was sufficient. No additional utility was required as the amount of reactants and products are small therefore heat recovery was not an issue in the lab-scale operation. However, in the large scale operation even to rise the HGO at 40°C , energy consumption is a big issue. Therefore while scaling up we have considered a heat integrated of CSTR process (Fig. 5) to reduce the overall energy consumption. The objective is to determine a retrofit design that can reduce the energy consumption, maximize energy recovery and minimize the capital investment. The exchangers, heaters and cooler are represented in Figure 5 by E, H and C respectively. The feed and product temperatures will be considered fixed and equal (T_{F0}). For simplicity we have used a simple CSTR model with the assumption of perfect mixing.

3.1 Process model

In Figure 5, feed stream S1 (cold stream) contains HGO and catalyst (HCOOH). They are mixed before preheating from T_{F0} to T_{F1} in heat exchanger E1. Then, the mixture is fed into heater H₁ to preheat from T_{F1} to reaction temperature (T_r). The stream leaving the reactor S3 (hot stream) is divided into two streams (S4 and S5) according to the splitter ratio (S_r). Stream S3 is cooled from T_r to T_0 by in contact with feed stream S1 through heat exchanger E1. Stream S4 is cooled from T_r to T_{01} by oxidant stream S2 in heat exchanger E2. The product streams (S3 and S4) are mixed and cooled to T_{F0} in

cooler (C) by using utility water at T_{w1} . The model equations for the whole process are shown in Figure 6. There are thirty four equations and forty four variables (forty unknown and four specified) and seventeen fixed parameters (shown in Table 1) in these equations. T_{F0} , T_{w1} , T_s and V_0 are specified and ΔT_2 , ΔT_4 , T_r , T_{w2} , τ and S_r are relaxed and optimized.

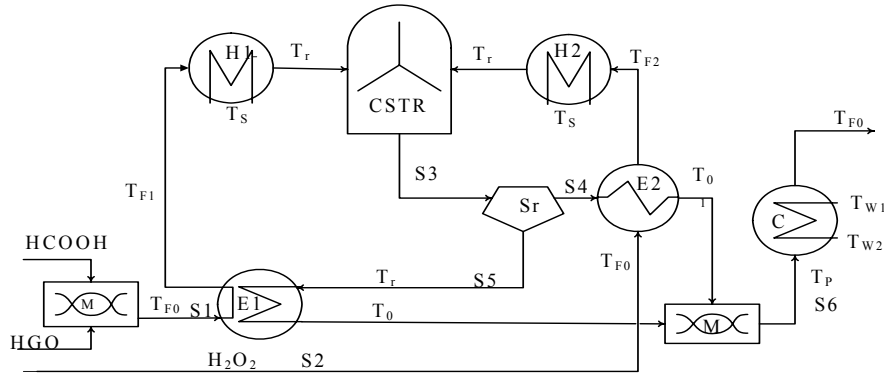


Fig.5. Process flowsheet of heat - integrated reaction system

4. Optimization Problem Formulation

The optimization problem can be described as follows:

| | |
|------------|---|
| Given | feed and product temperature (T_{F0}), steam temperature (T_s), water temperature (T_{w1}) and volumetric flow rate of feed (V_0); |
| Optimize | residence time (τ), reaction temperature (T_r), outlet temperature of cooled water (T_{w2}), splitter ratio (S_r), minimum approach temperatures (ΔT_2 , ΔT_4) |
| So as to | |
| Minimize | the total cost of the process (C_t) including capital investment |
| Subject to | constraints on the conversion ($0.40 < X_A < 0.42$) and linear bounds on all optimization variables |

The objective function in the optimization problem formulation is the overall annual plant cost (C_t) that considers equipment cost (reactor C_d , heat exchangers C_E , pumping C_{PU}), and operating cost (C_0) (Fernando and Pedro, 1998). The correlations of C_d , C_E , C_{PU} and C_0 are shown in Figure 7.

$$C_t = C_d + C_E + C_0 + C_{PU} \quad (1)$$

The optimization problem is solved using gPROMS (2005).

5. Optimization Results

The results of optimization problem (summarized in Table 2) show that, the minimum total cost (C_t), amounts of steam and cooling water with heat integration of the oxidation process are less than those without the heat integration at specified variables ($T_{F0} = 300$ K, $T_{w1} = 298.15$ K, $T_s = 373.15$ K and $V_0 = 0.1$ m³/min). Furthermore the energy input without heat integration is 424% higher than that with heat integration of

the oxidation process. Note the minimum approach temperatures for the heat exchangers E1 and E2 (ΔT_2 and ΔT_4) are within 9-11 °K which is quite practical.

| | |
|---|---|
| <u>Heat Exchanger (E1)</u> | |
| $Q_{1E1} = (V_0\rho_H C_{PH} + V_0\rho_F C_{PF})(T_r - \Delta T_1 - T_{F0})$, $\Delta T_1 = T_r - T_{F1}$, $\Delta T_2 = T_r - T_{F0}$ | |
| $Q_{2E1} = S_r(V_0\rho_H C_{PH} + V_0\rho_F C_{PF} + V_0H_2\rho_{H2}C_{PH2})(T_r - (T_{F0} + \Delta T_2))$, $Q_{1E1} = Q_{2E1}$ | |
| $\Delta T_{lm1} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)}$, | $A_{E1} = \frac{Q_{1E1}}{U_E \Delta T_{lm1}}$ |
| <u>Heat Exchanger (E2)</u> | |
| $Q_{1E2} = (1 - S_r)(V_0\rho_H C_{PH} + V_0\rho_F C_{PF} + V_0H_2\rho_{H2}C_{PH2})(T_r - (T_{F0} + \Delta T_4))$, $\Delta T_4 = T_{01} - T_{F0}$ | |
| $Q_{2E2} = V_0H_2\rho_{H2}C_{PH2}(T_r - \Delta T_3 - T_{F0})$, $Q_{1E2} = Q_{2E2}$ | |
| $\Delta T_3 = T_r - T_{F2}$, $\Delta T_{lm2} = \frac{\Delta T_3 - \Delta T_4}{\ln\left(\frac{\Delta T_3}{\Delta T_4}\right)}$, | $A_{E2} = \frac{Q_{1E2}}{U_E \Delta T_{lm2}}$ |
| <u>Heater (H1)</u> | <u>Heater (H2)</u> |
| $Q_{H1} = (V_0\rho_H C_{PH} + V_0\rho_F C_{PF})\Delta T_1$ | $Q_{H2} = (V_0H_2\rho_{H2}C_{PH2})\Delta T_3$ |
| $Q_{S1} = M_{S1}\lambda$, $A_{H1} = \frac{Q_{H1}}{U_H \Delta T_{lmH1}}$ | $Q_{S2} = M_{S2}\lambda$, $A_{H2} = \frac{Q_{H2}}{U_H \Delta T_{lmH2}}$ |
| $Q_{H1} = Q_{S1}$, $\Delta T_{lmH1} = \frac{(T_S - T_r) - (T_S - T_{F1})}{\ln\left(\frac{T_S - T_r}{T_S - T_{F1}}\right)}$ | $Q_{S2} = Q_{H2}$, $\Delta T_{lmH2} = \frac{(T_S - T_r) - (T_S - T_{F2})}{\ln\left(\frac{T_S - T_r}{T_S - T_{F2}}\right)}$ |
| <u>Cooler (C1)</u> | |
| $Q_C = (V_0\rho_H C_{PH} + V_0\rho_F C_{PF} + V_0H_2\rho_{H2}C_{PH2})(T_P - T_{F0})$, $Q_C = M_w c_{pw}(T_{w2} - T_{w1})$ | |
| $\Delta T_{lmC} = \frac{(T_P - T_{W2}) - (T_{F0} - T_{W1})}{\ln\left(\frac{T_P - T_{W2}}{T_{F0} - T_{W1}}\right)}$, | $A_C = \frac{Q_C}{U_C \Delta T_{lmC}}$, $T_P = (S_r T_0 + (1 - S_r) T_{01})$ |
| <u>CSTR</u> | |
| $X_A = \frac{-r_A \tau}{C_{A0}}$, $F_{A0} = v C_{A0}$, $C_A = C_{A0}(1 - X_A)$, $-r_A = A e^{-E/RT} C_A$ | |

Fig.6. Model equations of heat - integrated reaction system

Table 1. Nominal and values of constant parameters used in the model

| | |
|---|---|
| Initial concentration, C_{A0} , mol/ m ³ = 33.3 | Activation energy, E, J/mol = 7622 |
| Arrhenius Factor, A, min ⁻¹ = 0.2279 | Heat capacity of H ₂ O ₂ , C_{PH2} , J/kg K = 3 517 |
| Density of H ₂ O ₂ , ρ_{H2} , kg/m ³ = 1400 | Heat capacity of HGO, C_{PH} , J/kg = 1988.73 |
| Heat capacity of HCOOH, C_{PF} , J/kg = 1730 | Heat capacity of water, C_{pw} , J/kg = 4181.3 |
| Density of HGO, ρ_H , kg/m ³ = 817 | Density of HCOOH, ρ_F , kg/m ³ = 1220 |
| Gas constant, R, J/mol K = 8.314 | Latent heat, λ , J/kg = 2256918 |
| Over all heat transfer coefficient for exchanger U_{E1} , U_{E2} W/m ² K = 321 | |
| Over all heat transfer coefficient for heater, U_{H1} , U_{H2} , W/m ² K = 851 | |
| Over all heat transfer coefficient for cooler, U_C , W/m ² K = 638 | |

Table 2. Results of optimisation problem

| | With heat integration | Without heat integration | Decision variable type | Optimized value |
|-------------------------|-----------------------|--------------------------|------------------------|-----------------|
| A, m ² | 133 | 66.15 | ΔT_2 , K | 9.128 |
| C _i , \$ | 53965 | 84454.7 | ΔT_4 , K | 11.200 |
| CS*, % | 36 | 0.0 | S _r , % | 0.5149 |
| M _S , kg/min | 2.30 | 12.47 | τ , min | 44 |
| M _W , kg/min | 178 | 356.46 | Tr, K | 343.467 |
| MCR, kJ | 5212 | 2.21E04 | T _{w2} , K | 305.15 |
| MER, kJ | 5212 | 2.21E04 | X _A | 0.410 |
| MHR, kJ | 1.71E04 | 0.0 | ----- | ----- |
| ES, % | 77 | 0.0 | ----- | ----- |

*CS = Cost saving, MCR= Minimum cooling requirement, ES= Energy saving, MER= Minimum energy requirement, MHR= Maximum heat recovery

$$C_d, \$ / yr = 4.18 \left(\frac{900}{280} \right) \left(\frac{937.7}{3} \right) \left(\frac{V}{\pi} \right)^{0.6227}$$

$$\log_{10} C_E = K_1 + K_2 \log_{10} A + K_3 (\log_{10} A)^2$$

$$C_o, \$ / yr = \frac{900}{760} (7896 - 6327 q + 47640 q^2 - 10220 q^4)$$

$$C_{pu}, \$ / yr = \left(\frac{900}{834} \right) \left(\frac{38.6}{3} \right) (264.2 F_{A_0})^{0.8050}$$

Where: K₁ = 4.8306, K₂ = -0.8596, K₃ = 0.3187, A is the total heat exchanger surface area, m², V is the reactor volume, m³ and q = (Q_H+Q_C)/Q^N and Q^N=2.54*10⁷ J/min.

Fig.7 Correlation for different cost functions.

6. Conclusions

The removal of DBT from model oil and total sulfur from heavy gas oil by oxidative desulfurization in a small batch reactor with hydrogen peroxide have been investigated using formic acid as the catalyst. The effectiveness of sulfur removal is found to be proportional to reaction temperature in the range of 40 to 60 °C. The sulfur removal of DBT-containing model oil can reach 40-98% under different reaction temperatures.

To combat high energy demand for a large scale oxidation process, a heat integrated CSTR system is considered. Using optimization techniques within gPROMS, minimum energy input, maximum heat recovery and minimum investment and operating cost are determined. The results show that the cost and energy savings are in the range of 36% and 77% respectively.

7. References

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