Catalytic Oxidation of Mercaptans in Light Oil Sweetening: Kinetics and Reactor Design

Sudip K. Ganguly[a,*], Gautam Das[a], Gautam Kumar[b] , Sunil Kumar[a] , Bir Sain[a], Madhukar O. Garg[a]
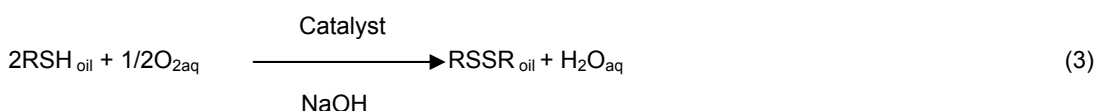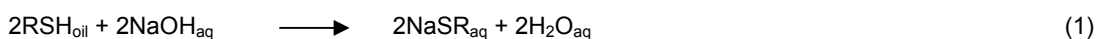
[a]CSIR - Indian Institute of Petroleum, Dehradun, 248005, India
[b] Department of Chemical Engineering, Lehigh University, Pennsylvania, 18015, USA
sganguly@iip.res.in

Design of an oxidizer in Light Oil Sweetening process requires established rate kinetics. With the development of a novel sulphonamide catalyst, the need to establish its rate kinetics was felt necessary. Our earlier studies on mechanistic kinetics established that the rate law was similar to single substrate Michaelis-Menten kinetics. In our present study, batch reactor data was simulated based on total reaction time to predict optimum catalyst dosage and contact time in the oxidizer for industrial scale operations. Feed mercaptide concentration to an oxidizer in the refineries generally falls in the range of 0.05-0.15 mol L^{-1}. Thus, kinetic studies were conducted with a feed having mercaptan concentration 0.138 mol L^{-1} at 15, 30 and 45^{0}C to cover industrial process conditions. The catalyst concentration was varied in the range of 25-200 ppm. Effective activation energy was estimated as 13.97 kJ mol^{-1} which compared well with 16 kJ mol^{-1} obtained from our earlier studies and 12 kJ mol^{-1} reported by Xia et al. (1999) for oxidation of mixed thiols.

1. Light Oil Sweetening

Lighter petroleum products like liquefied petroleum gas (LPG) and light straight run naphtha (LSRN) usually contains light mercaptans (RSH). These are undesirable due to their foul odour and highly corrosive nature. Presence of light RSH also affects the activity of catalyst used in the downstream processing of these petroleum products. The process of converting thiols by catalytic oxidation to less deleterious disulfides is known as sweetening (Basu et al., 1993). The light RSH present in LPG and LSRN are first extracted with aqueous caustic solution to form sodium mercaptides (NaSR) as shown in eq. (1) and subsequently are oxidized in the presence of a catalyst and air to organic disulfides (RSSR) in the oxidizer represented by eq. (2). The overall reaction may thus be represented by eq. (3).

$$2RSH_{oil} + 2NaOH_{aq} \longrightarrow 2NaSR_{aq} + 2H_2O_{aq} \tag{1}$$

$$2NaSR_{aq} + H_2O_{aq} + 1/2O_{2aq} \longrightarrow 2 NaOH_{aq} + RSSR_{oil} \tag{2}$$

$$2RSH_{oil} + 1/2O_{2aq} \xrightarrow[\text{NaOH}]{\text{Catalyst}} RSSR_{oil} + H_2O_{aq} \tag{3}$$

2. Development of Sweetening Catalyst

The catalyst plays an important role in oxidation of mercaptides to disulphides. Thiol oxidation mechanism in the presence of transition metal complexes was studied by Wallace et al. (1964). Cobalt phthalocyanine disulphonate is commonly used as commercial catalyst in extractive sweetening of LPG and lighter petroleum fractions. The dusty nature of this catalyst caused handling problems. To improve this, tetrasulphonate form of catalyst was developed which was highly soluble but had lower activity.

Accordingly, in our effort to develop superior sweetening catalysts for extractive sweetening; our attention was particularly drawn towards the amide group, which could further improve solubility of catalyst in aqueous alkaline medium. Thus, a novel cobalt phthalocyanine sulphonamide catalyst (Thoxcat ES) was indigenously developed (Sain et al., 2004a & 2004b). To ascertain the commercial usefulness of this catalyst its activity and stability were evaluated. Thoxcat ES was found to be better in activity and comparable in stability as compared to the commercial catalyst. The details of its synthesis, characterization and performance are detailed elsewhere (Das et al., 2009).

3. Light Oil Sweetening Kinetics Studies

Industrial use of Thoxcat ES catalyst in oxidizer for an extractive sweetening process for LPG and LSRN would require a kinetic model. Thus, kinetics studies were carried out using 1-butanethiol as model compound which represent light RSH in LPG and LSRN (Ganguly et al., 2011). A semi-batch type reactor was selected for kinetics study due to its ability in regulating the flow rate of one of the reactants (oxygen), so that the kinetics of the process could be studied more effectively. The semi-batch reactor was specifically selected for its advantages such as simplicity in design, compactness, and homogeneous mixing leading to good temperature control that are essential for kinetic studies.

3.1 Experimental Setup
The schematic diagram of the experimental setup is shown in Figure 1. As shown the semi-batch reactor (11) made up of glass with a sintered glass distributor (9) at the bottom to uniformly distribute the gas flow was used for the study. It was jacketed to maintain the desired reaction temperature within +/- 0.2^0C by circulating water from a thermostatic bath (12). The rubber septum (8) was used for collecting samples of reaction mixture with the help of syringes. The reproducibility of data was within +/- 1%. Oxygen for thiol oxidation was supplied by air from an air cylinder (1) and was introduced from the bottom of the column in an up flow mode and was measured by a calibrated manometer (5), which was crosschecked by a wet gas flow meter (4). Nitrogen from cylinder (15) was purged to inertise the bubble column reactor before the start of the reaction. 250 mL of 10 wt % sodium hydroxide solution was poured in the reactor (11) along with nitrogen purging to remove dissolved oxygen and to maintain an inert atmosphere. 1-Butanethiol was then introduced into the reactor (11) through the septum (8) using a syringe to achieve desired RSH feed concentration. A sample was withdrawn from this reaction mixture after sufficient mixing to measure the feed RSH concentration. Calculated amounts of Thoxcat ES required to maintain a catalyst concentration level from 25 to 200 ppm in the reaction mixture was introduced through the same septum (8). Nitrogen purging was further continued to ensure proper mixing and then it was changed to air with the help of a three-way valve (6). The start of air flow marked the zero time for the reaction. The colour of the reaction mixture, which was initially dark greenish black, changed to light blue colour at the completion of the reaction representing total reaction time. Experimental conditions were selected such that mass transfer resistance was minimum (van de Vusse, 1958) and thus intrinsic kinetics could be determined (Lavric & Cerato-Noyerie, 2012). Mercaptide conversions at t = 1 min were plotted at 15^0 C and 45^0 C as a function of airflow rates to cover the entire range of experimental studies. The trend showed that conversions did not change much above airflow rate 1.1 dm^3 min^{-1} at 45^0C and 1.2 dm^3 min^{-1} at 15^0 C. Thus, all kinetic studies were conducted above 1.2 dm^3 min^{-1} to ensure diffusion free regime (Ganguly et al., 2011 & 2012).

3.2 Mechanistic Kinetics
Mercaptide concentration in feed to an oxidizer of extractive sweetening unit in the Indian refineries generally falls in the range of 0.05 - 0.15 mol L^{-1}. The kinetic studies were conducted with a feed RSH concentration of 0.138 mol L^{-1} of 1-butanethiol at 15, 30 and 45^0C as function of reaction time, t to cover industrial process conditions (Ganguly et al., 2011). In all these experiments Thoxcat ES concentration was maintained at 200ppm.The concentration profiles were fitted to a polynomial expression by regression as shown in eq. (4).

$$C_{RSH} = a + bt + ct^n \qquad (4)$$

Experimental RSH consumption rate was computed as in eq. (5)

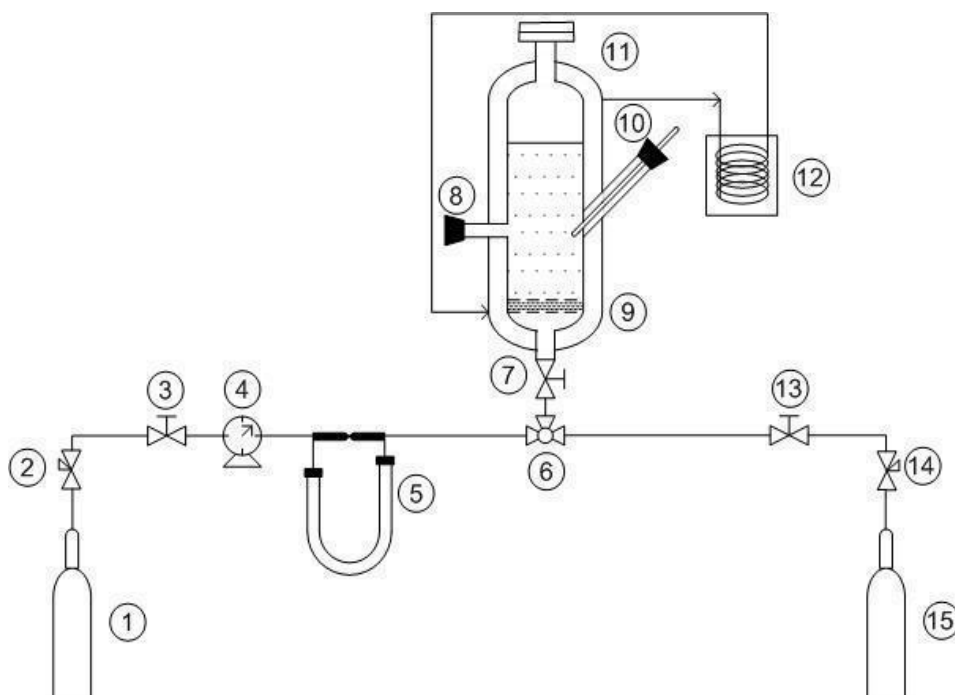$$\frac{dC_{RSH}}{dt} = -r_{RSH} = b + nct^{n-1} \qquad (5)$$

Figure 1: Schematics of the Experimental Setup. Components: 1, air cylinder; 2 and 14, pressure regulator valves; 3, 7 and 13, valves; 4, wet gas flow meter; 5, manometer; 6, three-way valve; 8, septum; 9, sintered glass; 10, thermometer 11, reactor; 12, thermostatic water bath; 15, nitrogen cylinder.

In our studies on mechanistic kinetics of thiol oxidation (Ganguly et al., 2011 & 2012) it was established that the rate law derived followed the double substrate Michaelis-Menten kinetics shown in eq. (6).

$$-r_{RSH} = \frac{k_2 k_3 k_4 [cat]_{tot}[C_4H_9SH][O_2]}{[k_{-2}(k_4+k_{-3})+k_3k_4[O_2]+k_2(k_4+k_{-3})[C_4H_9SH]+k_2k_3[C_4H_9SH][O_2]]} \qquad (6)$$

During experiments, oxygen was present in excess which was identical to conditions prevailing in the industrial scale oxidizers. Considering the availability of excess oxygen than required stoichiometrically at constant airflow rates; the rate expression was reduced to single substrate Michaelis-Menten kinetics shown in eq. (7).

$$-r_{RSH} = \frac{k_1^I [cat]_{tot}[C_4H_9SH]}{[K_M+[C_4H_9SH]]} \qquad (7)$$

The parameters of the mechanistic rate law were estimated (Ganguly et al., 2011 & 2012) with the help of experimental rates calculated using eq. (5).

3.3 Total Reaction Time

As mentioned earlier, it is well known that 150-200 % of stoichiometric oxygen requirement is always available in industrial oxidizers; therefore the rate law in eq. (7) is applicable to industrial oxidizers. In this study, an alternate method for determination of kinetic parameters was explored. The method is based on total reaction time. Using the simplified rate law, expression for total reaction time was derived. For relatively high K_M values reported in our earlier studies (Ganguly et al., 2011), Michealis-Menten rate expression in eq. (7) was simplified to the following linear form:

$$-r_{RSH} = k_{eff} [cat]_{tot} [C_4H_9SH] \qquad (8)$$

where,

$$k_{eff} = \frac{k_1^I}{K_M} = \frac{k_{01}^I}{K_M} e^{\frac{-E_{eff}}{R.T}} = k_{0eff}.e^{\frac{-E_{eff}}{R.T}}$$

For a given temperature, catalyst concentration, and air flow rate, k_1^I and K_M are constant therefore, k_{0eff} may be considered as constant. Thus eq. (8) was simplified to effective rate law as shown in eq. (9)

$$-r_{RSH} = k_{0eff}.[cat]_{tot} \, e^{\frac{-E_{eff}}{R.T}} \, [C_4 H_9 SH] \tag{9}$$

Expression for total reaction time, t_r for light mercaptans was obtained based on eq. (9)

$$t_r = \frac{\ln (C^0_{RSH}/C_{RSH})}{[cat]_{tot} \, k_{eff}} \tag{10}$$
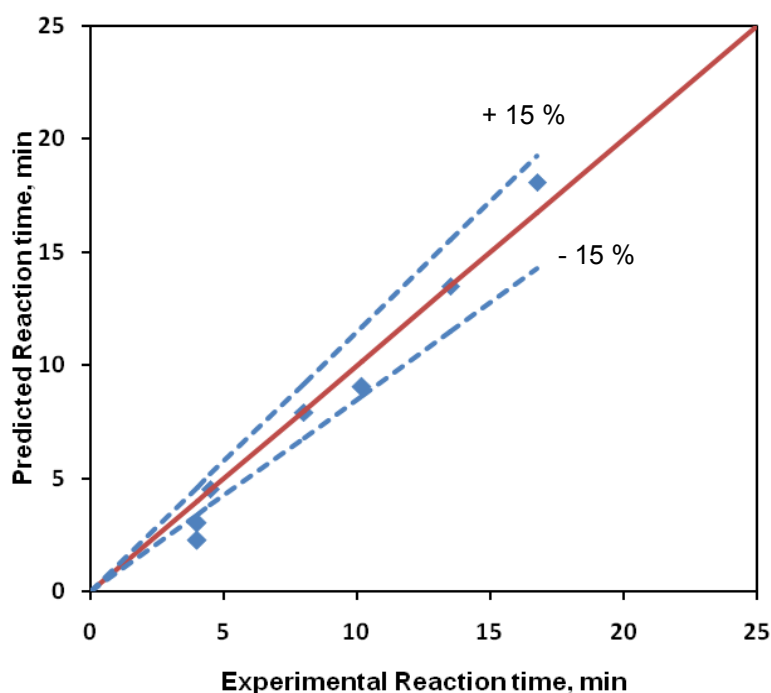
4. Result and Discussions

The experimental total reaction time obtained for different catalyst concentrations and temperature conditions are reported in Table 1. The data on concentration effect was used to estimate the parameters at a constant temperature. Whereas, data at different temperatures were used for estimating the effective activation energy. A Nedler-Mead Simplex optimization procedure was adopted for minimization of objective function Δ_d shown in eq. (11). Effective activation energy (E_{eff}) was estimated as 13.97 kJ/mol from Arrhenius plot which compared, well with our earlier studies (16 kJ/mol) and reported by Xia et al.,(1999) (12 kJ/mol) for oxidation of similar mixed thiols. The effective rate law for Thoxcat ES is shown in eq. (12). The kinetic parameters estimated were used to predict the reaction time. The predicted values of reaction time have been compared with experimental reaction time in the parity plot shown in Figure 2.

$$\Delta_d = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \frac{(t_r^{exp} - t_r^{pre})^2}{(t_r^{exp})^2}} \tag{11}$$

$$-r_{RSH} = 3.395 \times 10^6. \, e^{\frac{-13972}{R.T}} \, [cat]_{tot}.[C_4 H_9 SH] \tag{12}$$

Table 1: Experimental Reaction Time

[cat]$_{tot}$ ppm	C^0_{RSH} mol L^{-1}	T K	t_r^{exp} min
25	0.138	303	16.75
50	0.138	288	13.50
50	0.138	303	10.17
50	0.138	317	8.00
100	0.138	303	4.50
150	0.138	303	4.00
200	0.138	303	4.00

Figure 2: Parity plot for Reaction time.

The dotted lines represents the +/- 15 % boundaries of deviation. It is evident that most of the points fall within this boundary indicating a reasonably good fit.

4.1 Effect of Catalyst concentration on Contact time

To scale up the process to an industrial scale, expression for reaction time was interpreted as contact time, τ for flow reactors as shown in eq. (13) and the liquid hold-up is represented by $(1 - \varepsilon_g - \varepsilon_p)$. Where, fraction occupied by gas hold up and packing are represented by ε_g and ε_p respectively.

$$\tau = \frac{\ln{(C^0_{RSH}/C_{RSH})}}{[cat]_{tot}\, k_{eff}\,(1 - \varepsilon_g - \varepsilon_p)} \tag{13}$$

The effect of catalyst concentration on contact time in a liquid-liquid industrial oxidizer with a liquid hold-up ranging from 0.40 to 0.60 has been simulated. As mentioned earlier, in Indian refineries, mercaptide concentration in feed generally falls in the range of 0.05-0.15 mol L^{-1}. Simulations were therefore done at three different mercaptan concentrations to cover the entire range. Results obtained are reported in Table 2. The trend showed that the effect of catalyst concentration is marginal above 150 ppm over the entire feed range. Hence, a catalyst dosage of 150 ppm may be considered as optimal. Contact time was decided based on rate controlling conditions. Since, 0.15 mol L^{-1} is the heaviest feed and 288 K is usually the lowest operating temperature, the reaction rate was expected to be the slowest and therefore controlling. Accordingly, for liquid hold-up ranging from 0.40 to 0.60 with optimum 150 ppm catalyst dosage, predicted contact time was observed to fall in the range of 14–20 min. Therefore, based on simulations, it will be reasonable to recommend 20 min as the optimum contact time for near complete conversion of mercaptides in an industrial oxidizer.

4.2 Commercial Experience

Considering that the catalyst is better in activity and comparable in stability with established kinetics commercial viability needed to be established as the next step. The process for catalyst preparation was scaled up from a 50 g lab level to 50 kg in commercial plant.This catalyst was tried in four different Indian refineries. In all the cases the catalyst dosage was kept at 200–225 ppm with feed mercaptide to oxidizers varying in the range of 0.10–0.15 mol L^{-1}. It was able to achieve product mercaptan levels below 10 ppm.

Table 2: *Effect of Catalyst concentration on Contact time*

[cat]$_{tot}$ ppm	C^0_{RSH} = 0.05 mol L^{-1}			C^0_{RSH} = 0.10 mol L^{-1}			C^0_{RSH} = 0.15 mol L^{-1}		
	Contact time, min								
Temp, K →	288	303	318	288	303	318	288	303	318
25	77-115	58-86	44-66	81-121	60-90	47-70	83-124	62-93	47-70
50	39-58	29-43	22-33	40-60	30-45	24-35	42-62	31-47	24-36
100	19-29	15-22	11-17	20-30	15-23	12-18	21-31	16-23	12-18
150	13-20	10-15	8-11	14-20	10-16	8-11	14-20	11-16	9-12
200	11-17	9-12	7-10	12-17	9-13	7-10	13-18	9-13	8-10

During the plant trials, Thoxcat ES performance confirmed lesser catalyst consumption than the commercial one while maintaining desired mercaptan level in the treated LPG. Moreover, it is cheaper than available commercial catalysts. Thus, industrial trial runs validated the salient conclusions of this kinetics study. The catalyst was later commercialized in seven Indian refineries namely; Indian Oil Corporation Limited, Digboi, Bharat Petroleum Corporation Limited, Mumbai, Hindustan Petroleum Corporation Limited, Mumbai , Visag and Bhatinda, Reliance Industries Limited, Jamnagar and Mangalore Refinery and Petrochemicals Limited, Mangalore. Moreover, the catalyst can be used in conventional as well as in fiber film sweetening processes.

5. Conclusions

The salient conclusions from this study are as follows:

(a) The following simplified rate law based on total reaction time was proposed for catalytic oxidation of 1-butanethiol:

$$-r_{RSH} = 3.395 \times 10^6 \cdot e^{\frac{-13972}{R.T}} [cat]_{tot}.[C_4 H_9 SH]$$

 (b) Thoxcat ES dosage is important as it decides the operating cost; thus simulations were carried out to determine optimum catalyst dosage and found to be 150 ppm.

(c) The optimum contact time based on reaction rate at the lowest operating temperature for the heaviest feed at optimum catalyst dosage of 150 ppm was found to be 20 min.

(d) Industrial trial runs validated the salient conclusions of this kinetics study.

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