

Removal of Mercaptance from Diesel

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Abstract. Mercaptants are not desirable in petroleum products, because it corrode the combustion engine and also liberate oxides of sulphur, which are dangerous for health of living things and environment. Thus, its removal is very necessary from the petroleum crude and petrolatum products. In the present work, extraction of C_6H_5SH was performed in batch reactor at atmospheric pressure and low temperature. Extract used was 0.1 mole NaOH individually and along with cobalt pthalocynine (Pc). During the studies 17.32, 27.63, 32.45 and 35.45 % mercaptant conversion (chemical extraction) were obtained at 40, 45, 50, 60 °C respectively without MPc in 90 minutes. The conversion were found to increased using CoPc. 61.0, 65.0, 82.1 and 83.2 % with CoPc catalyst in same time. These results confirm that synthesized catalysts enhanced the reaction rate and the catalytic activity increased with temperatures. The reaction rates constant were found to 0.005, 0.0075, 0.0084, 0.0088 min^{-1} at temperature 40, 45, 50, 60 °C respectively in absence of catalyst, which were enhanced to 0.0104 and 0.012 at temperatures 40 and 45 °C with the CoPc catalyst. For CoPc catalyst at 50 °C and 60 °C, two step mercaptant conversion was noticed. First fast followed by slow in second step, In first step the rate constant were 0.032 and 0.060 min^{-1} at 50 and 60°C, while it were 0.015 and 0.0169 min^{-1} at same temperatures in the second step.

Keywords: Mercaptants removal, cobalt pthalocynine, extraction, kinetics, sweetening process

1. Introduction

Due to very stringent international norms of sulfur contains in petroleum products, it is great challenge to petroleum and petrochemical industries to remove sulfur from it. Sulfur is not desirable due to its harmful effect to environment, thus, it need to treat before sending to market. There are many commercially viable sweetening processes, which are listed in Table 1 [1].

Table 1: List of various sweetening Process

Caustic wash	Chelate sweetening
Doctor treatment	Merox process
Hypochlorite wash	Mercapfining
Solutizer and Dualayer process	Hydrofining/hydrotreating
Copper chloride sweetening	Lead sulfide sweetening
Inhibitor sweetening	Unisol treating
Sulfuric acid treating	Bender-Petresco
Vapor-phase clay treatment	Molecular sieves

The most common practice is to extract to mercaptants in alkali and oxidize to disulphides with air in the presence of a catalyst called merox process [2]. For this metal Phthalocyanines (Pc) are widely used as catalysts to remove mercaptants present in the form of aromatic or/and aliphatic form. Alkaline solution (dilute NaOH) has been found to very effective to extract the mercaptants chemically. The extraction cum oxidation of mercaptants found to increase in presence of metal pc.. Various metals like cobalt [3], iron [4],

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manganese [5, 6], molybdenum [7], and vanadium [8] are used with phthalocyanines. The mercaptant removal from LPG using Co-ph tetrasulphonamide has been reported by Das et al [9].

In the present work, CoePc were synthesized in the glass reactor in the laboratory. This catalyst was used to Extraction of C₆H₅SH content in diesel. The effect of temperature on chemical extraction at different temperate was studies. The rate constants were also evaluated.

2. Material and Methods

2.1. Material

The chemicals used were L.R grade. NaOH, 1-2-4 benzenetricarboxylic were obtained from Merk Private Limited Mumbai. Phenol red, Sodium methoxide, Urea 1,2,4 – Trichlorobenzene and thalic anhydride were arranged from LOBA Chemie Pvt. limited, Mumbai. The magnetic stirrer used for catalytic synthesis was Remi, India made. The batch rector used for experiment was fabricated by K. C. Engineers Ambala, India. The catalyst was synthesized in glass reactor in batch mode and extraction of mercaptance was performed in S. S. reactor in batch mode. The marcaptant present was determined by titration with sodium methoxide using phenol red indicator.

2.2. Methods

2.2.1. Synthesis of cobalt phthalocyanine

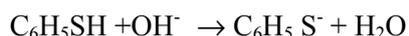
In a three neck 500 ml glass reactor 17.64 g of phthalic anhydride, 18 g urea, 1 g of ammonium molybdate, 8.0 g of cobalt chloride hexa hydrate and 300 ml of trichlorobenzene was taken. Glass reactor was equipped with necessary equipment such as a stirrer, reflux condenser, and temperature measuring device. The resulting mixture was stirred for 1 hour at temperature of 110⁰C, and subsequently stirred for 6 hours at temperature of 120⁰C. The mixture was cooled to about 100⁰C. 400 ml of hot water of about 60⁰C was then gradually added to the reaction mixture, and further stirred for 2 to 3 hours with refluxing. The mixture (solid slurry mass) was washed with about 3 litre of hot water to remove the chemical that not take part in reaction. The filtered solid residue was dried at 110⁰C and grinded in laboratory grinder. The grinded partials were used for reaction.

2.2.2. Phenol mercaptant removal process

250 ml diesel containing calculated amount of thiophenol was taken in 1.5 liter s.s. reactor. In this reactor 250 ml 0.1 N NaOH was taken, thus total amount of liquid is 500 ml. The extraction process was started by constant stirring at settled temperature i.e. 40, 50, 55 and 60⁰C. At a time intervals of 10, 20, 30, 45, 60, and 90 minutes the reactor was stopped and allow the interface to form between the two layers namely extract layer at the top comprising of diesel and un extracted thiophenol and raffinate layer at bottom comprising of NaOH and extracted mercaptan group. Sample of 10ml was taken from the top layer i.e. disel and titrated with sodium methoxide using phenol red indicator.Amount of mercaptans extracted was calculated sticometerilly.

3. Result and Discussions

When the diesel containing C₆H₅SH stirred with alkali, the C₆H₅SH from diesel is extracted by NaOH and the reaction take place is.



The rate of removal of C₆H₅SH from the diesel and simultaneously conversion of C₆H₅SH to C₆H₅ S⁻ is represented by first order reaction with respect C₆H₅SH (A).

Thus, rate equation can be written as: $-dC_A/dt = kC_A$

Where A= C₆H₅SH

k=first order rate constant

The reactive extraction process was found to increase in presence of catalyst. The amount (molar) C₆H₅SH initially contain in reactor was determined. Then at time intervals, amount of C₆H₅SH contain in reactor decreased due to extraction of it by NaOH and conversion of extracted C₆H₅SH to C₆H₅ S⁻. The

remaining C_6H_5SH contain in the reactor at that time was determined by titration and corresponding conversion was estimated.

The Fig. 1 and 2 show the % conversions of mercaptans (SH) to S^- achieved at different temperatures and at different times. Cobalt Pc was found to be effective catalyst with maximum conversion attained at 60 °C of 83.2% in 90 minutes. The maximum of 35.25% obtained in absence of catalyst. The conversions increased when the time was gradually increased for catalytic and non catalytic reactive extraction process. The 17.32, 27.63, 32.45 and 35.45 % conversion of mercaptant was obtained at 40,45, 50 and 60 ° in 90 minutes without the catalyst. In same time 61.0, 65.0, 82.1 and 83.2 % conversion were obtained using CoPc catalyst. Beyond the 90 minutes is the rate of conversion was not significant and remained constant around the values obtained at time 90 minutes.

Fig. 3 and 4 show the plot of first order reaction rate kinetics to find the rate constants of extraction of C_6H_5SH and conversion of it to $C_6H_5S^-$ with and without catalyst. From the figures it may be seen that the slope of graph increased with temperate, thus, rate constant increased with temperature. The rate constants of 0.005, 0.0075, 0.0084, 0.0088 min^{-1} were obtained at temperature 40, 45, 50, 60 °C respectively in absence of catalyst, which were increased to 0.0104, 0.012 min^{-1} at temperatures 40, 45 respectively with the CoPc catalyst. For CoPc catalyst at 50 °C and 60 °C, two step mercaptant conversion was noticed. First fast followed by slow in second step, In first step the rate constant were 0.032 and 0.060 min^{-1} at 50 and 60°C, while it were 0.015 and 0.0169 min^{-1} at same temperatures in the second step.

4. Conclusions

i. During the studies 17.32, 27.63, 32.45 and 35.45 % mercaptant extraction and conversion were obtained at 40, 45, 50, 60 °C respectively using 10% NaOH

ii. 61.0, 65.0, 82.1 and 83.2 % merpcatant extraction and conversion was obtained using 10 % NaOH and CoPc (0.5 g/l) in same time.

iii. First order Reaction rate constants were found to fit the process without catalyst and with CoPc catalyst. The rate constant evaluated were 0.005, 0.0075, 0.0084, 0.0088 min^{-1} at temperature 40, 45, 50, 60 °C respectively in absence of catalyst, which were enhanced to 0.0104 and 0.012 at temperatures 40 and 45°C with the CoPc catalyst.

For CoPc catalyst at 50 °C and 60 °C, in first step the rate constant were 0.032 and 0.06 min^{-1} , while it were 0.015 and 0.0169 min^{-1} at same temperatures in the second step.

iv. The result shows that Co pc catalyst is effective for extraction and conversion of mercaptant present in petroleum fraction

5. References

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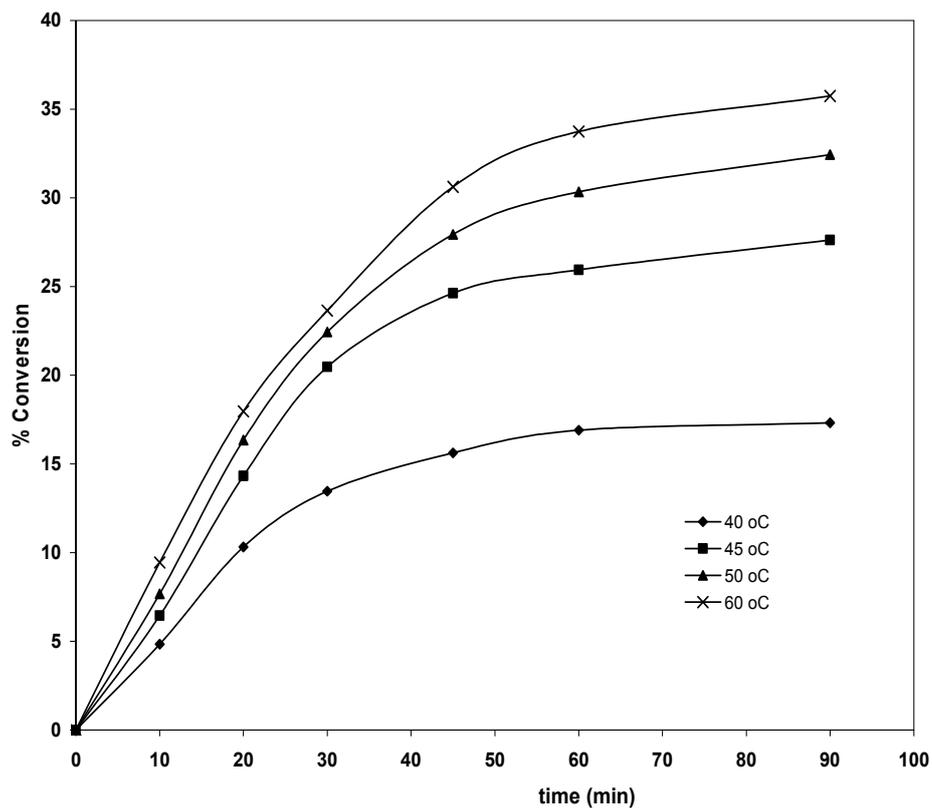


Fig. 1: Conversion of thiophenol without catalyst. SHi=0.948 gm/l

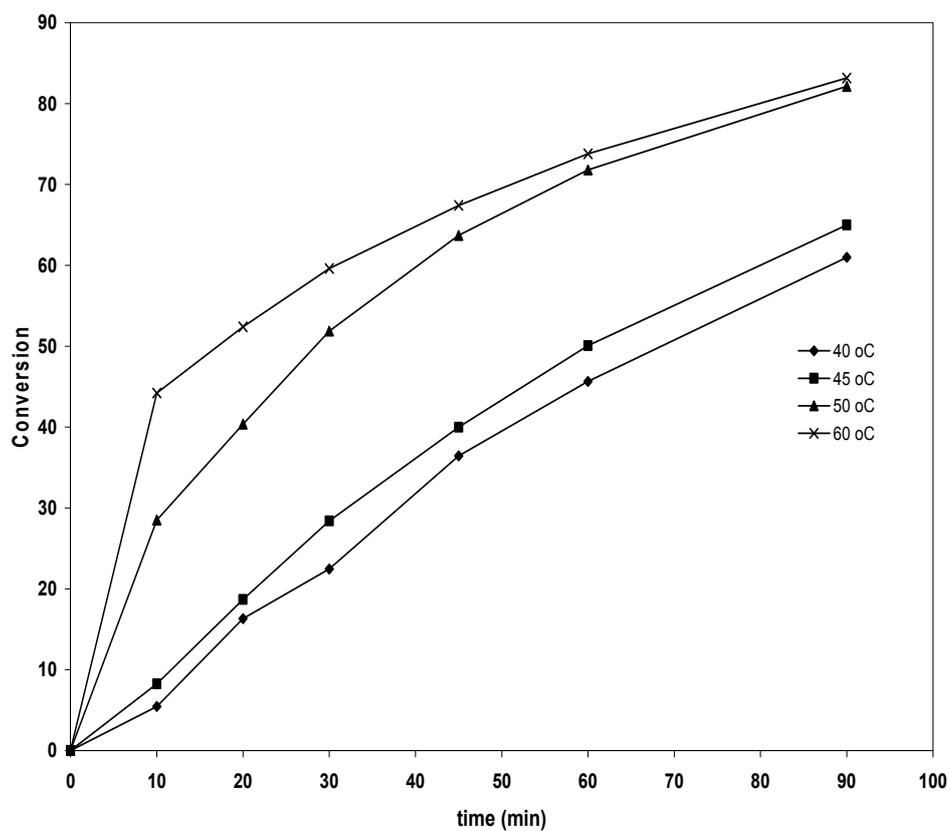


Fig. 2: Conversion of thiophenol with CoPc catalyst. SHi=0.948 gm/l

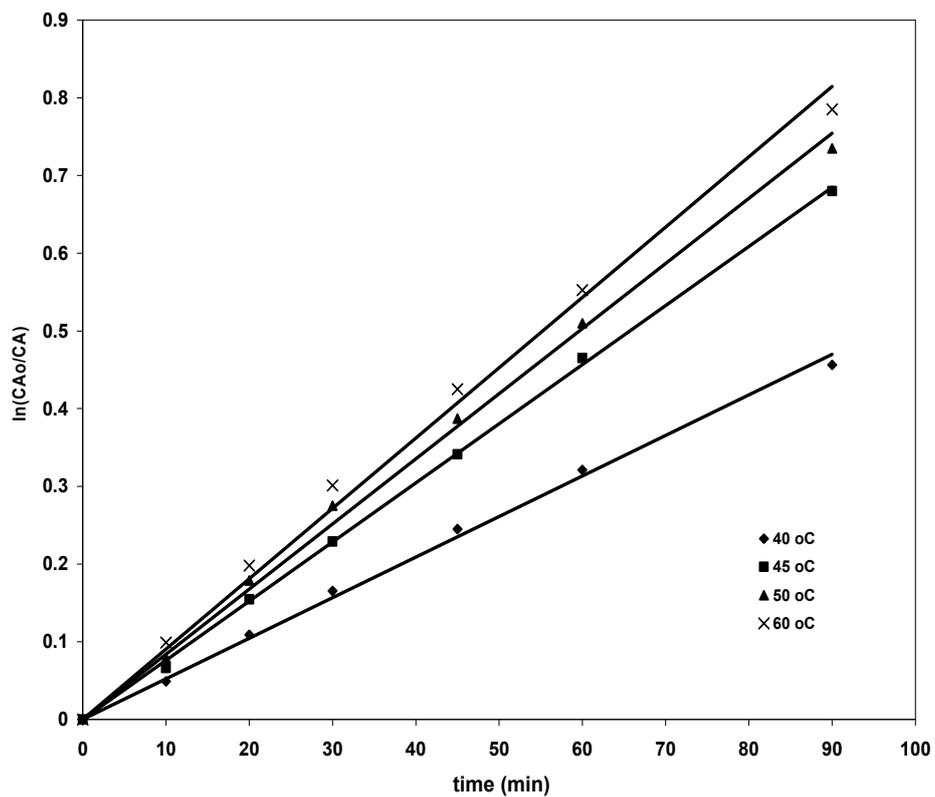


Fig. 3: Plot for rate constant evolution for conversion of thiophenol without catalyst

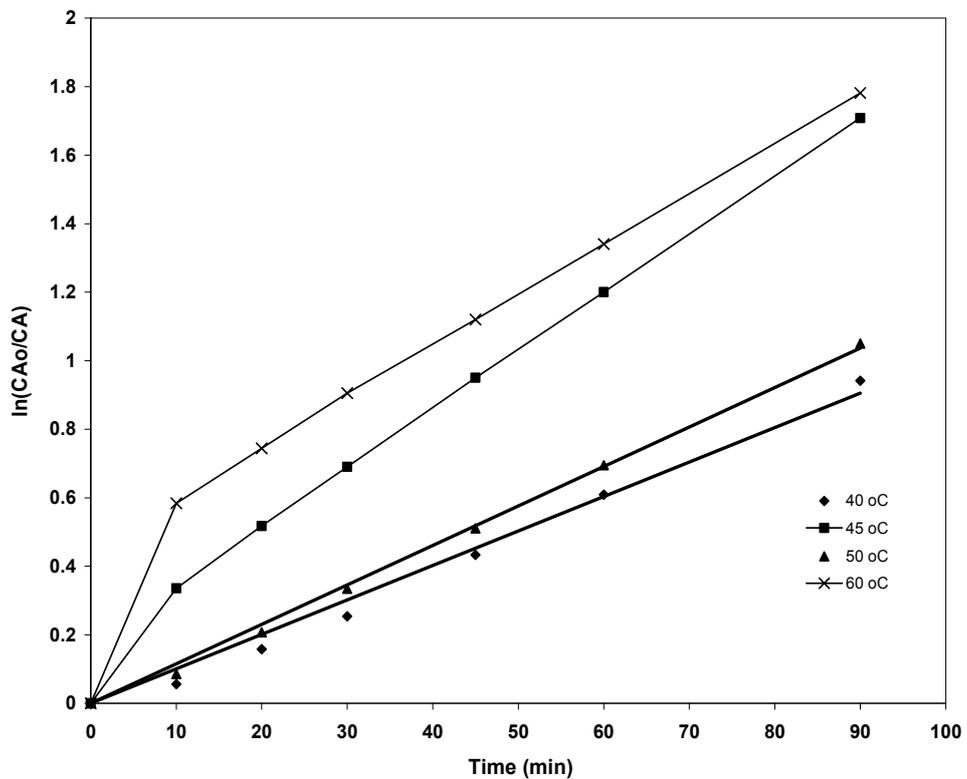


Fig. 4: Plot for rate constant evolution for conversion of thiophenol using CoPc catalyst