Feasibility studies of Green LPG sweetening catalyst

PROJECT REPORT

As a part of the requirement for the partial fulfillment of the course work of AcSIR

CSIR-Harnessing Appropriate Rural Interventions and Technologies (HARIT)

Candidate
Sudip K Ganguly
AcSIR Enrollment no:
20EE18J19011

Submitted to:
Dr Shailendra Tripathi
AcSIR HARIT Coordinator
CSIR Indian Institute of Petroleum (IIP)

Supervisors:

Dr. Anjan Ray
Advisor
Director, IIP
Dehradun

Prof C. B. Mazumdar
co-Advisor
Deptt. of Chem. Engg.
IIT Roorkee

Feasibility studies of Green LPG sweetening catalyst

Submitted as a part of the requirement for the partial fulfillment of the course work of CSIR-Harnessing Appropriate Rural Interventions and Technologies (CSIR-HARIT) for the award of the degree of PhD

भापेसं
Creating Future Fuels

Advisor: Prof. Anjan Ray, Director, IIP

Co-Advisor: Prof. C. B. Mazumdar, Deptt. Of Chem. Engg., IIT Roorkee

Submitted by – Sudip K Ganguly
Sweetening Area
Chemical & Material Synthesis Division
CSIR-Indian Institute of Petroleum, Dehradun 248 005

Declaration – I Sudip K Ganguly, hereby certify that the work presented in this Report entitled "**Feasibility studies of Green LPG sweetening catalyst**" in partial fulfillment of the course requirement for award of the Degree of Ph.D., being submitted to CSIR-HARIT Unit, CSIR-Indian Institute of Petroleum, Dehradun, is an authentic record of Project Research work carried out by me at CSIR –Indian Institute of Petroleum, Dehradun during the period January to May 2019 and under the supervision of Prof. Anjan Ray, Advisor.

Date 7/6/19

SK Ganguly
Signature of the Student

Date 17/6/19

Signature of the Advisor

Table of contents

1. Introduction:

The Indian government has introduced a scheme known as Pradhan Mantri Ujjwala Yojna (PMUY) for safeguarding the health of women and children in the villages [1]. The PMUY aims to provide ten crore LPG unit connections to these households situated in villages over the next few years so that cooking is possible in such households using a clean fuel like LPG. This is aimed at improving the quality of life for villagers, especially mothers who need to spend most of the time in their kitchens developing lungs issues due to excessive smoke in the conventional systems. The aim is to cover most of the rural sectors of the country. With the new government in place, strong efforts are being made to make it more popular and accessible to the rural masses and increase the number of beneficiaries.

LPG sweetening is a popular and widely used commercial process worldwide in petroleum refineries for the conversion of mercaptans [2]. The homogeneous catalyst plays an important role in the sweetening process. Hence, increased demand for LPG would increase consumption of sweetening catalyst as well, which creates a need for developing a cost competitive catalyst. The acceptability of LPG sweetening catalyst in a refinery for its regular use is usually based on five criterions, i.e., LPG product quality, activity, stability, carryover characteristics, and operating cost. The higher activity is reflected in terms of lower catalyst consumption as well as reduced frequency of catalyst dosage, which is translated to reduced operating cost on a day to day basis. In turn, also gets reflected as better LPG on spec product and lower mercaptide levels in the regenerated caustic stream being recycled to the LPG extractor top [3].

Additionally, the catalyst needs to be robust enough, which is interpreted in terms of catalyst stability. However, on the contrary, even while meeting the product LPG spec criterion with required activity, the catalyst might also lead to higher carryover tendencies. Thus, there is a need to optimize the catalyst recipe in such a way so that we obtain the desired activity and stability for on-spec LPG with minimum instances of carryovers during its use in operations. Accordingly to cater to the needs of both low-cost options of catalyst synthesis to make it popular amongst the rural initiatives like HARIT as well as the Make in India initiatives to commercialize the catalyst worldwide [4] a greener catalyst was synthesized and its feasibility was established.

2. Need for a green sweetening catalyst:

Given this need, IIP-BPCL has developed a globally competitive sweetening catalyst named Thoxcat ES. Sustained efforts from CSIR-IIP and BPCL to improve and extend acceptance resulted in the commercialization of this catalyst in 10 Indian Refineries so far [3, 5]. In continuation, our focus now shifted to the M.E. since 2015, which holds 15-20% of the global sweetening catalyst demand. It has been observed that the configuration of sweetening plants in the M.E. is unique. The oxidizers are normally designed to handle multiple rich caustic phases coming from more than one extractor bottoms. In the Indian refineries, the oxidizers process only a single rich phase thereby leading to lesser variation in mercaptide loads (usually not more than 10000 ppm w). However, this is not the case with the M.E. refineries. The carryover issue is aggravated when a mixture of more than one rich mercaptide streams is handled by a common oxidizer which is not only high but has fluctuating mercaptide levels. Such conditions are commonly encountered in the M.E. refineries [6-8]. Often this leads to sudden variation in mercaptide levels and flows which results into the peaking of mercaptide levels (may touch 25000 ppm w) and might be one of the factors leading to extreme foaming conditions resulting in more frequent carryover issues observed from the downstream disulfide separator stack. This might get further aggravated by the effects of process operating parameters like superficial gas velocity, caustic strength, catalyst concentration, and temperature [7].

Thus the catalyst selection criterion of M.E refineries is stringent. The catalyst is selected only when the catalyst not only meets the LPG specs and consumption requirements but the one which has minimum instances of carryover. With this present problem in mind, it was thought of designing a new catalyst which has a less foaming tendency and yet active. It was thought that in the process we should synthesize a catalyst which is green and has less foaming tendency. We thought of new chemistry which would lead to a different substitution, i.e., something different to the existing sulphonamide group. The present report presents our work and its feasibility studies in this direction. It discusses the economics and possible future improvements for its commercialization.

3. Synthesis of the green catalyst:

The following procedure was adopted during the synthesis of the ammonium salt of sulfonated - Co (II) Pc (greener route):

Cobalt phthalocyanine (0.5 g) was slowly added with stirring to 6-fold excess by weight of chlorosulphonic acid. The mixture was then heated to 104 °C for four h under continuous stirring. The reaction mixture was then cooled first to room temperature and then chilled by adding ice. Dropwise addition of ammonia was done with precautions to the mixture as the reaction was highly exothermic until the desired pH (~11-12) was achieved. After this, the mixture was left overnight on stirring, followed by evaporation of the solvent to get the desired catalyst. The solid was separated, ground and dried at 70 ^{0}C under vacuum; yield (0.80g). The catalyst was characterized using IR. The spectrum is shown in **Figure 1 (a)** which is original, and **Figure 1 (b),** which is re-plotted for clarity. The trend matches with the signature IR spectra for cobalt phthalocyanine [9]. The substitutions of NH_4^+ presence is indirectly evidenced by N-H stretching at 3223 cm^{-1} and the presence of SO_3^- is indirectly evidenced by S=0 stretching at 1402 cm^{-1}. The existence of the macrocyclic structure of the porphyrinic ring is evidenced by the peak at 630.8 cm^{-1}.

The present method is an improvement over our earlier method (cobalt phthalocyanine tetra sulphonamide) wherein sulphonyl chloride use has now been eliminated, making the process greener, cheaper, and less energy intensive [10].

4. Experiments on foamability studies:

The foamability aspect is being used as an important criterion for the screening of catalyst in the M.E. Accordingly; we have benchmarked the performance of the present catalyst against the one which is already successful in the industry. An experimental set up was designed to estimate the foamability behavior of the catalyst and comparison with an established catalyst used as a reference.

4(a) Experimental set-up

An experimental set up was created to study the foaming tendencies of the catalytic thiol oxidation process. A column set up fitted with sintered glass (Grade 1) at the base connected with a gas flow meter for introducing air with quantified air flow was fabricated. The system was set to represent near industrial conditions to arrive at a logical conclusion.

4 (b) Experimental Procedure

A calculated amount of Thoxcat ES catalyst sample required for maintaining a catalyst concentration of in the range of 200 ppm was dissolved in 14 wt% NaOH solution used as the representative feed to the oxidizer. The mixture of NaOH and catalyst solution was poured in the jacketed glass column reactor maintained at around 40^0 C under nitrogen atmosphere. The desired amount of ethanethiol to make initial mercaptide concentration 16500 ppmw was injected in the reaction mixture along with nitrogen purge for a few minutes for thoroughly mixing of the thiols in the mixture. The gas flow was then quickly changed from nitrogen to air. This marked the zero time of the mercaptide conversion reaction. The flow rate was adjusted to 0.2 LPM to have near industrial conditions. The color of the reaction mixture was initially found to be dark brownish black at the start of the reaction. The completion of the reaction was indicated by the appearance of a light blue color. The time needed for complete conversion and foamed heights were noted. The results of these experimental runs have been reported in **Table 1**.

The catalyst was compared with the standard catalyst **R-15011** under feed conditions similar to the M.E. refinery operating conditions. The data is reported in **Table 1**. The performance data with the standard catalyst without additives is also reflected in **Table 1 and Fig (s) 2-5**. Results indicate that even with a comparable activity, the foamability is markedly reduced, i.e., more than 50%. **Further, the activity is acceptable as it falls within the 20 to 31 minutes reaction time range.**

5. Experiments on catalyst stability:

The stability of the catalyst was tested under rugged conditions by use of a feed containing 750 ppm of hexane thiol in petroleum ether at 25 ^{0}C. 100 ml of this feed was taken and contacted with 20 ml of alkaline phase containing 89 ppm of the catalyst dissolved in it. The contacting was carried out in a round bottom flask of 250 ml volume under stirred condition (1000 rpm) for 10 mins. The hydrocarbon phase was decanted, and fresh 100 ml of feed was contacted with the same catalyst containing alkali phase repeatedly has also been shown in **Table 2**. A total of 1.2 L of petroleum ether was contacted in both the studies under identical experimental conditions. The mercaptan content in the hydrocarbon phase was monitored by standard UOP 163-89 method using Metrohm Titration Unit (888 Titrando). The experiments were repeated for both the catalysts under identical conditions, and the results are reported in **Table 2**. It was found that the mercaptan level was 5 ppmw for the existing catalyst; however, for the new formulation, the levels varied between 16 to 33 ppmw indicating a need for stability improvement by optimizing synthesis conditions.

6. Economics of the synthesis procedure:

A cost comparison was made to find out how much reduction in the cost per batch would it be there considering that there is a change in the processing step. The quantity of the raw material needed for the production of a standard batch of 45 kg was compared. The estimated quantities of raw materials required for its synthesis are shown in **Table 3.** The costing on prevailing rates was computed and compared.

The comparison shows that the proposed improved process would cost 12-15% cheaper and also would be produced faster with reduced batch processing time. This is expected to reduce the energy requirements by roughly 5-7% leading to savings in the energy cost of the same tune.

7. Conclusions and Recommendations:

- The use of this new catalyst proves that the substituent group has a marked effect on the formability of the catalyst. The foamability was reduced by more than 50%, which is well within the acceptance criterion.
- The cost of synthesis of this in the industrial level would be at least 12-15% cheaper than the original recipe using the sulphonamide group with savings of 5-7% on energy consumption. The green catalyst would subsequently lead to less chemical effluents and less chemical wastage during industrial synthesis and lab evaluation studies.
- The ammonium salt of the sulfonated CoPc is greener with comparable activity and much lower foamability. It thus looks feasible with respect to the M.E. market.

Recommendations

Though the activity of the new catalyst is comparable with much-reduced foaming tendencies, however, **the stability at present is lower than the existing product; though it can be improved by playing with the chlorosulphonation temperature and time for its further optimization.** Hence we must try several series of the catalyst up to chlorosulphonation of 150^0 C (starting from 104 ^{0}C) and must undergo stability tests of the fine-tuned catalyst. **The catch is synthesizing the new catalyst without compromising on the activity part.**

Acknowledgments

I acknowledge the efforts and cooperation of the SCP/CMSD team (Dr. Suman L Jain) and Dr. P K Khatri) in developing the greener catalyst which was evaluated in SWT/CMSD Lab with the help of my colleague Shri Sunil Kumar. I am thankful to my advisors Prof Anjan Ray (Director, IIP) and Prof C B Mazumdar (Deptt of Chem Engg. IIT Roorkee) for their advice and continuous guidance. I express my gratitude to Sh. Raghuvir Singh, TO of FTIR group in ASD for the IR analysis. Finally, I express my sincere thanks to AcSIR Coordinator, Dr. S Tripathi for his cooperation and suggestions.

Appendix

Table 1: Comparative performance of different catalysts w.r.t foaming

A	B	C	D	E	F	G	H
S No.	Catalyst Code	Additive type	Reaction time (min)	Initial liq. Ht. (cm)	Final liq. Ht. (cm)	Net frothing obs. (cm) (G-F)	Remarks
1.	Thoxcat-ES wet cake **(without additive)**	**Nil**	**20**	19	52	**33**	**Baseline**
2.	IIP Ref Thoxcat ES R-15011 **(with additive)**	**Silicon**	**31**	25	40	**15**	**Reference**
3.	Ammonium salt-based catalyst **(without additive)**	**Nil**	**25**	29	40	**11**	**Activity and Foaming tendencies acceptable**

Table 2: Stability comparison of the catalysts

S.No	The volume of feed processed, L Feed: Petroleum ether, 750 ppm	Existing catalyst 89 ppm	New catalyst 89 ppm
		Mercaptan level ppm	Mercaptan level ppm
1	0.1	5	16
2	0.2	5	16
3	0.3	5	16
4	0.4	5	16
5	0.5	5	17
6	0.6	5	17
7	0.7	5	17
8	0.8	5	17
9	0.9	5	17
10	1	5	33
11	1.1	5	23
12	1.2	5	29

Table 3: Comparison of raw material quantity used for catalyst synthesis

S.No	**Components**	**Existing catalyst**	**New catalyst**
		Quantity, kg	**Quantity, kg**
1	Cobalt Phthalocyanine	40	40
2	Chlorosulphonic Acid	250	250
3	Thionyl Chloride	100	0
4	Ammonia gas	50	50
5	Hydrochloric acid	7	7
6	Water washing	10000	10000
7	Ice	5000	5000
8	Water	400	400
9	NaOH	12.5	12.5
10	Additive (s)	40	8 (2+6)
11	**Total Batch cost**	97302	86342
12	**Cycle time**	**Seven days**	**Six and a half days**

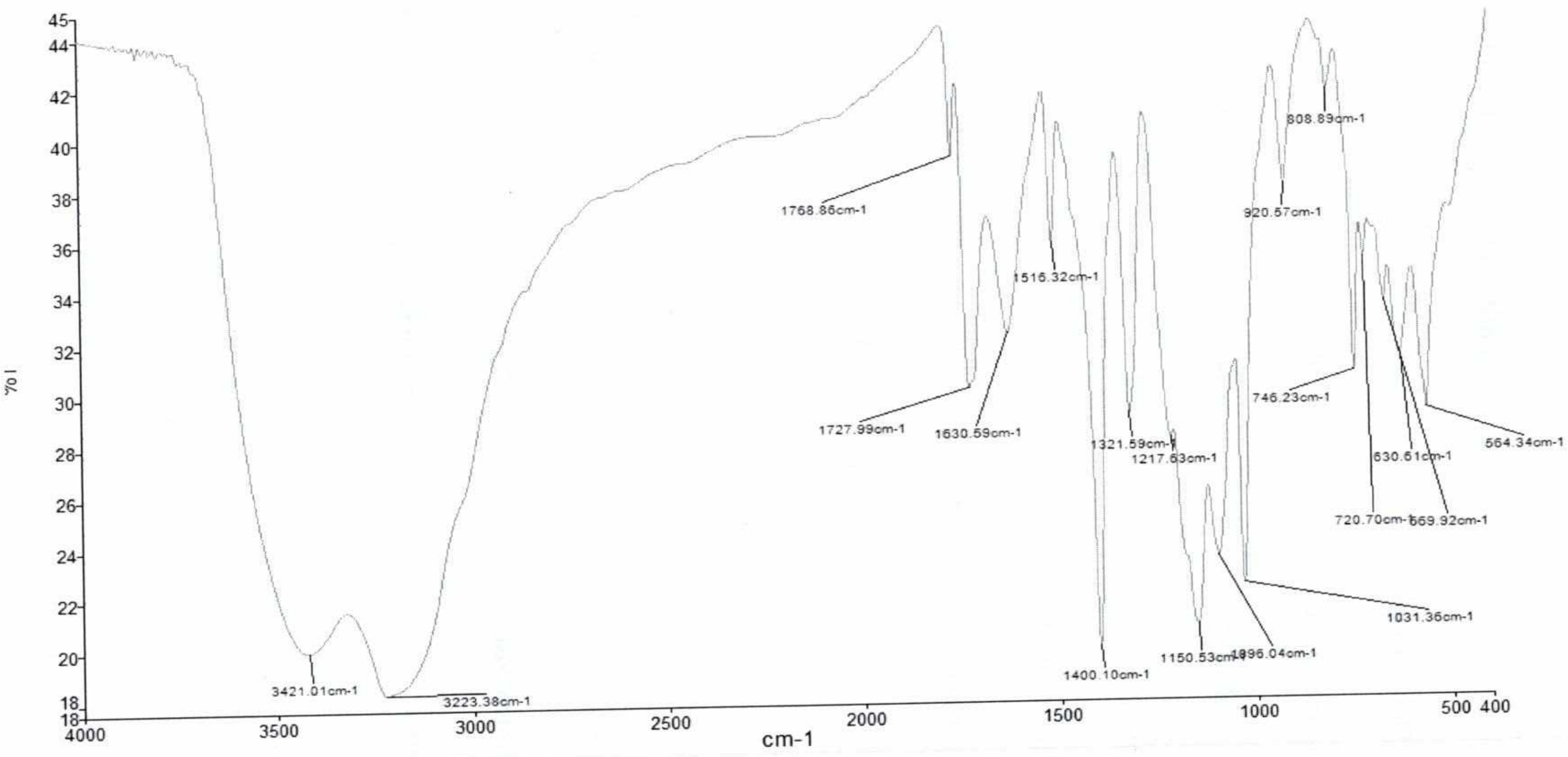

Figure 1(a): IR spectra of the Green Catalyst

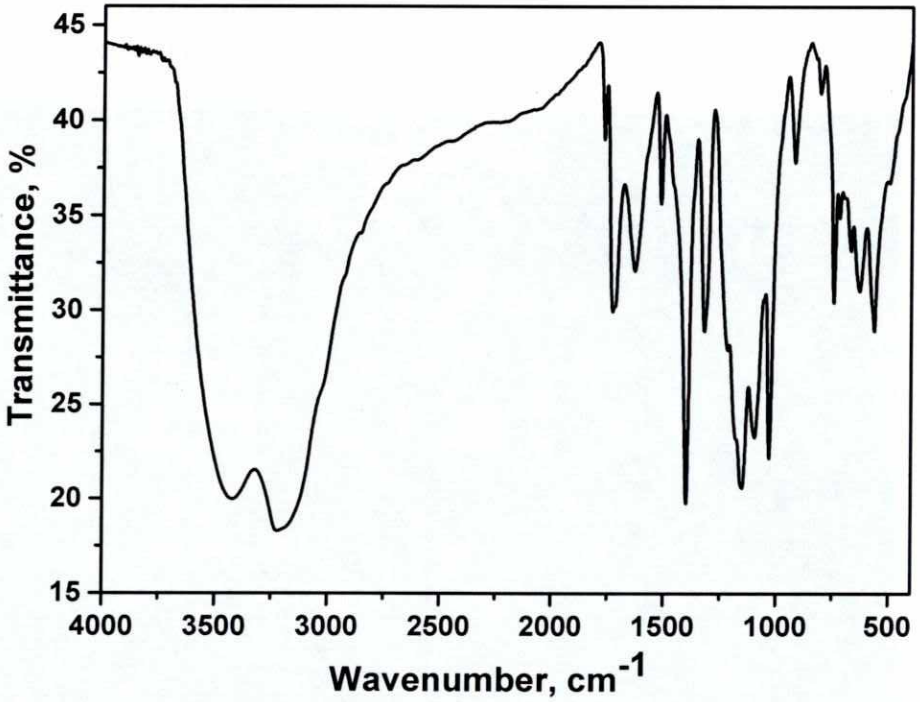

Figure 1(b): IR spectra of the Green Catalyst

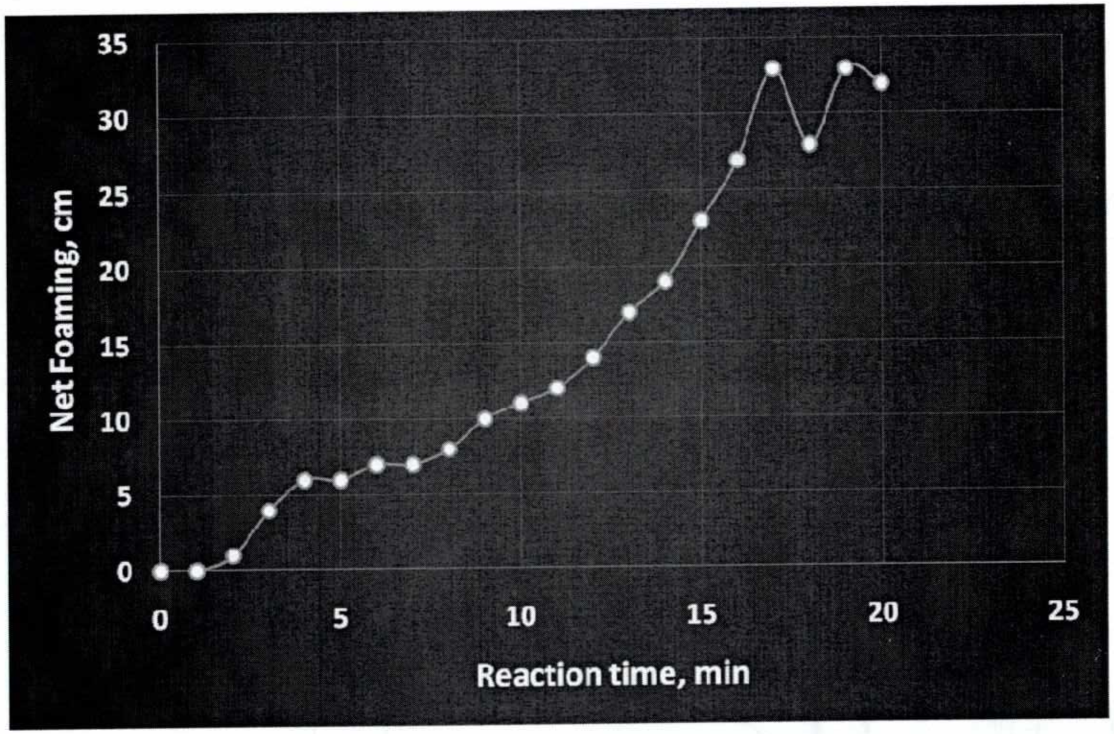

Figure 2: Foaming behavior using sulphonamide catalyst

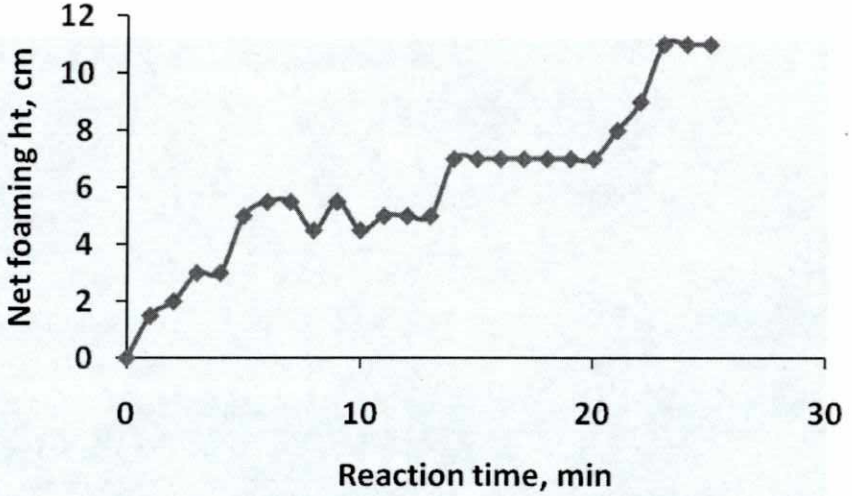

Figure 3: Foaming behavior using ammonium salt of sulfonated cobalt phthalocyanine catalyst

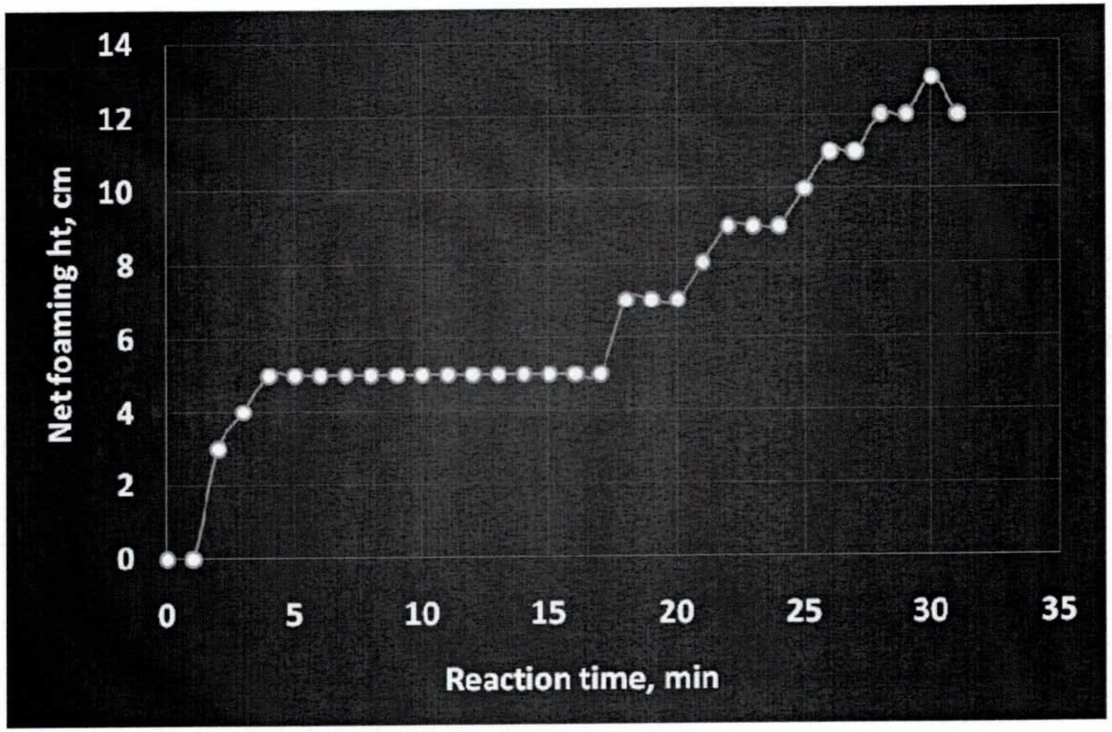

Figure 4: Foaming behavior using successful catalyst at commercial level R-15011

References:

[1] Pradhan Mantri Ujjwala Yojna from http://www.pmujjwalayojana.com accessed on 14th May 2018.

[2] B. Basu, S. Satapathy, A. K. Bhatnagar, Merox and related metal phthalocyanine catalyzed oxidation processes, *Catal. Rev.-Sci. Eng,* 1993, 35, 571-609.

[3] S. K. Ganguly, G. Das, S. Kumar, B. Sain & M. O. Garg, Mechanistic Kinetics of Catalytic Oxidation of 1- Butanethiol in Light Oil Sweetening. *Catal. Today*, 198(1), 246-251, 2012.

[4] Promotion of LPG Sweetening Catalyst, Thoxcat ES™ in the International Markets, Request for proposal to CSIR, 2019.

[5] S. K. Ganguly, G. Das, S. Kumar, B. Sain, M. O. Garg, Tune up sweetening process for your facility, *Hydrocarbon Proc.* 2013, 92 (6), 77–81.

[6] Report on ORPIC, Sohar visit by IIP-BPCL Team & Way forward, CSIR-Indian Institute of Petroleum Report no: RTD-126/2016, 2016.

[7] An Appraisal of Parametric Effects on the Kinetics of Frothing for Thoxcat ES, CSIR-Indian Institute of Petroleum Report no: CCD-137/2017, 2017.

[8] Performance evaluation of Thoxcat ES for ORPIC, Sohar Refinery, CSIR-Indian Institute of Petroleum Report no: CCD-130/2016, 2016.

[9] R. Seoudi, G.S.B. El-Bahy, Z.A. El-Sayed, FTIR, TGA, and DC electrical conductivity studies of phthalocyanine and its complexes, *J. Mol. Struc.* 2005, 753, 119-126.

[10] G. Das, B. Sain, S. Kumar, M. O. Garg, G. Murali Dhar, Synthesis, characterization and catalytic activity of cobalt phthalocyanine tetrasulphonamide in sweetening of LPG *Catal. Today,* 2009, 141, 152-156.