

Intensification and forecasting of low-pour-point diesel fuel production via modelling reactor and stabilizer column at industrial unit

N S Belinskaya, E V Frantsina, E D Ivanchina, N V Popova, I V Zyryanova and E V Averyanova

Department of Fuel Engineering and Chemical Cybernetics, National Research Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk, 634050, Russia
E-mail: belinskaya@tpu.ru, evf@tpu.ru

Abstract. In this work forecast calculation of stabilizer column in the technology of low-pour-point diesel fuel production was modelled. The results of forecast calculation were proved by full-scale experiment at diesel fuel catalytic dewaxing unit. The forecast calculation and full-scale experiment made it possible to determine the ways of mass transfer intensification, as well as to increase the degree of hydrogen sulphide removal in the column, and thereby to decrease corrosiveness of the product stream. It was found out that maintenance of the reflux rate in the range of 80–90 m³/h and injection of additional vapourizing streams, such as stable naphtha from distillation unit (in the volume of 10–22 m³/h) and hydrogen-containing gas (in the volume of 100–300 m³/h), ensure complete elimination of corrosive hydrogen sulphide from the product stream. Reduction of stream corrosive activity due to suggested solutions extends service life of equipment and pipelines at industrial catalytic dewaxing unit.

1. Introduction

Petroleum refining is a unique sector of industry in respect to corrosion. Virtually all known types of corrosion occur there due to the vast variety of operating conditions [1–5]. Every second failure at petroleum refineries is caused by corrosion of equipment [6].

The objective of this work is to decrease corrosive activity of stable naphtha, which is one of the products of diesel fuel catalytic dewaxing.

2. The subject of research and raw materials characteristics

Catalytic dewaxing unit is intended to produce summer, winter, and arctic diesel fuels (figure 1). Main production stages involve hydrotreating and dewaxing of the feedstock (mixture of atmospheric gas oil, straight-run diesel fractions, and visbreaking gasoline), stabilization of the product, and distillation with diesel fractions and stable naphtha production [7,8].

After unit start-up, high content of hydrogen sulphide in product stable naphtha was observed. It was discovered that hydrogen sulphide is formed in the bottom of the stabilizer column, as well as in the intermediate equipment at high temperature according to the reaction of mercaptane decomposition. Mercaptanes, in turn, are formed in the dewaxing reactor from olefins, which are the products of cracking reaction on dewaxing catalyst. The occurrence of mercaptane formation reaction in the dewaxing reactor was proved using thermodynamic analysis (the change in Gibbs free energy (ΔG) of this reaction is equal to $-69,1 \div -76,2$ kJ/mol).



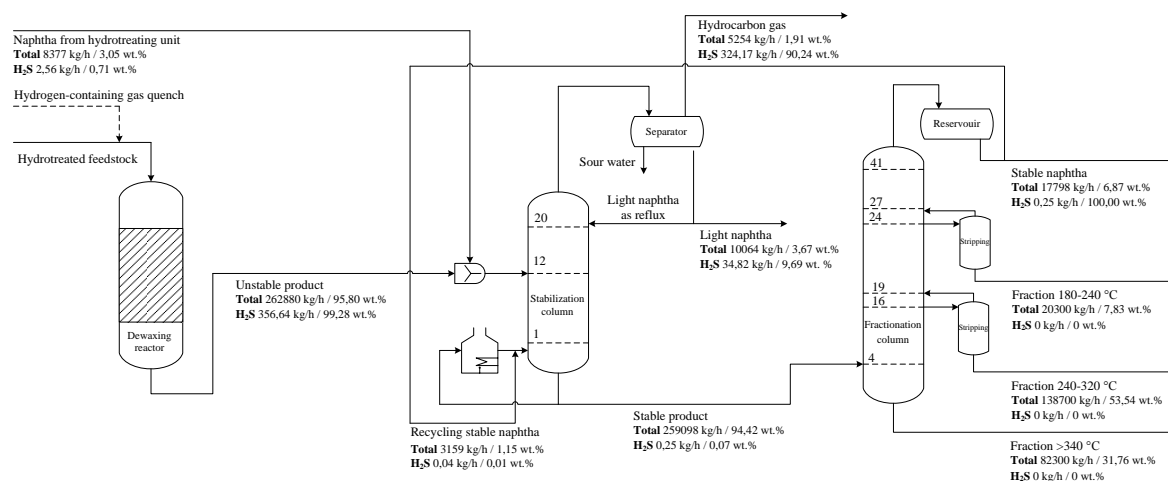


Figure 1. Industrial diesel fuels catalytic dewaxing unit

The bulk of hydrogen sulphide (96–99 wt.%) enters into the stabilizer column with unstable hydrogenate, which is the product of the reactor section. The rest of hydrogen sulphide (1–4 wt.%) enters into the stabilizer column with naphtha-distillate of hydrotreating unit.

It is known, that sulphur-containing compounds are distributed among the fractions according to chemical structure of hydrocarbons. Aliphatic compounds (low-molecular-weight mercaptanes, sulphides, disulphides) are presented in low boiling fractions. Thus, hydrogen sulphide concentrates in gas, light and stable naphtha. However, in compliance with the project of the unit, stable naphtha should be free from hydrogen sulphide.

The presence of hydrogen sulphide in product stable naphtha is harmful, since it causes corrosion of equipment located after distillation. The latter decreases equipment service life and enhances the probability of failure inception in the unit operation due to damage of equipment as a consequence of corrosion [9].

Hydrogen sulphide must be removed completely as a component of gas and light naphtha at the stabilization stage. However, the actual mode of stabilizer column operation does not provide total removal of hydrogen sulphide.

To achieve the objective of the work, the research on mass transfer intensification and hydrogen sulphide removal in the stabilizer column, as well as forecasting of low-pour-point diesel fuel production were conducted via modelling of the reactor and stabilizer column.

Study of any complex multi-stage petroleum refining process requires taking into account all production stages because of the fact that raw materials composition and technological parameters of previous stages influence significantly on the results of subsequent stages. The most effective method of research, forecasting, and optimization of petroleum refining processes is the method of mathematical modelling [10-12], applied in this work.

3. Results and discussion

To evaluate the influence of flow rates of reflux and recycled stable naphtha, entering the stabilizer column, the operation of industrial diesel fuel dewaxing unit was monitored.

Initially recycled stable naphtha was sent into the column through the furnace before November 2015. This limited its flow rate to 5 m³/h because of the pump power. As a result of column re-piping

(change of recycled stable naphtha direction for straight into the column by-passing the furnace) recycled stable naphtha flow rate was increased to 22 m³/h.

Thus, stable naphtha flow rate into the bottom of the column was increased from 2.2–4.2 to 17.0–22.0 m³/h after re-piping, which ensured decrease in hydrogen sulphide content in product stable naphtha from 0.0009–0.0015 to 0.0004–0.0008 wt.% (figure 2).

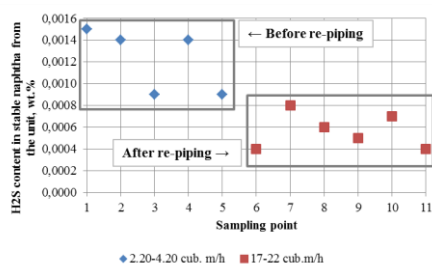


Figure 2. Impact of recycled stable naphtha flow rate increasing due to re-piping on hydrogen sulphide content in product stable naphtha

The monitoring of industrial dewaxing unit provided determination of dependency of hydrogen sulphide content in product stable naphtha on reflux and recycled stable naphtha flow rates. Thus, in case of reflux flow rate equal 76 m³/h (table 1), hydrogen sulphide content in product stable naphtha varies from 0.0009 to 0.0014 wt.% under change in recycled stable naphtha flow rate from 3.5 to 4.2 m³/h. The similar dependence is observed when dewaxing unit operated after re-piping. Thus, in case of reflux flow rate equal to 78 m³/h (table 2), hydrogen sulphide content in product stable naphtha varies from 0.0006 to 0.0008 wt.% under change in recycled stable naphtha from 20 to 22 m³/h.

Table 1. Hydrogen sulphide content in product stable naphtha before re-piping

| Date | Recycled stable naphtha flow rate, m ³ /h | Reflux flow rate, m ³ /h | H ₂ S in stable naphtha, wt.% |
|------------|--|-------------------------------------|--|
| 13.01.2015 | 2.20 | 79 | 0.0015 |
| 03.02.2015 | 4.20 | 72 | 0.0014 |
| 05.02.2015 | 4.20 | 71 | 0.0009 |
| 11.02.2015 | 3.80 | 76 | 0.0014 |
| 17.02.2015 | 3.50 | 76 | 0.0009 |

Table 2. Hydrogen sulphide content in product stable naphtha after re-piping

| Date | Recycled stable naphtha flow rate, m ³ /h | Reflux flow rate, m ³ /h | H ₂ S in stable naphtha, wt.% |
|------------|--|-------------------------------------|--|
| 23.11.2015 | 18 | 82 | 0.0004 |
| 25.11.2015 | 20 | 78 | 0.0008 |
| 26.11.2015 | 22 | 78 | 0.0006 |
| 27.11.2015 | 22 | 81 | 0.0005 |
| 30.11.2015 | 20 | 90 | 0.0007 |
| 07.12.2015 | 17 | 88 | 0.0004 |

Moreover, analysis of industrial data showed that hydrogen sulphide content in product stable naphtha depends on reflux flow rate. Thus, under constant recycled stable naphtha flow rate equal to 4.2 m³/h, and reflux flow rate equal to 71 and 72 m³/h respectively, hydrogen sulphide content varies from 0.0009 to 0.0014 wt.% (table 1). The similar correlation is observed when dewaxing unit operated after re-piping. Thus, under constant recycled stable naphtha flow rate, equal to 22 m³/h, and

reflux flow rate equal to 78 and 81 m³/h respectively, hydrogen sulphide content varies from 0.0005 to 0.0006 wt.% (table 2).

The developed mathematical model of diesel fuel dewaxing process, brought into coincidence with the model of stabilizer column (figure 3), ensured quantitative evaluation of reflux and recycled stable naphtha flow rates influence on hydrogen sulphide content in product stable naphtha.

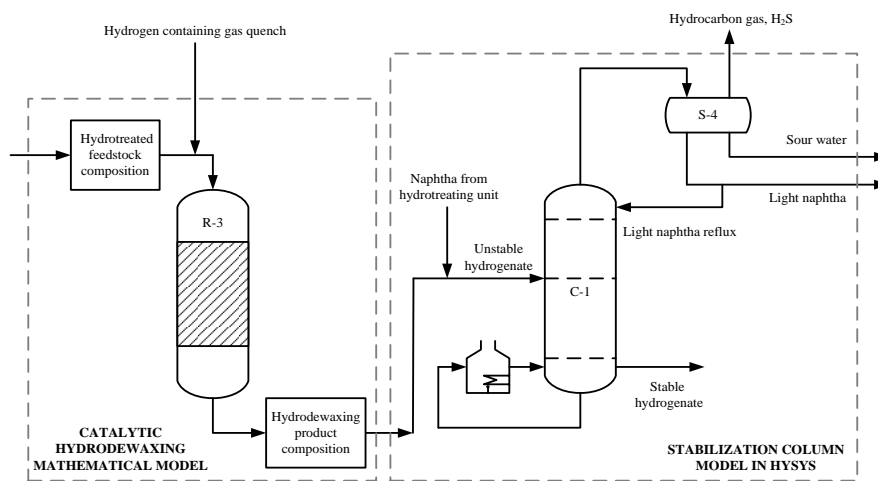


Figure 3. Schematic representation of reactor and stabilizer column joint operation for dewaxing process modelling

Calculation results are presented in figures 4-6.

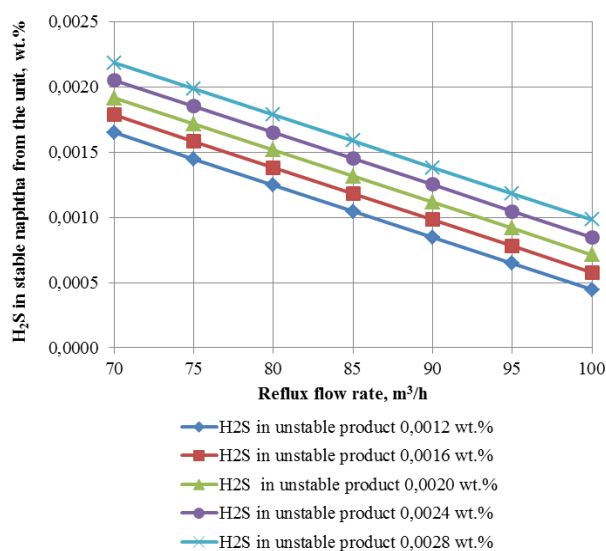


Figure 4. Impact of reflux flow rate on hydrogen sulphide content in product stable naphtha

As figure 4 shows, under increase in reflux flow rate into the column from 70 to 100 m³/h the content of hydrogen sulphide in product stable naphtha (stable naphtha from the unit) significantly declines from 0.0022 to 0.0005 wt.% depending on hydrogen sulphide content in the column feedstock (unstable product).

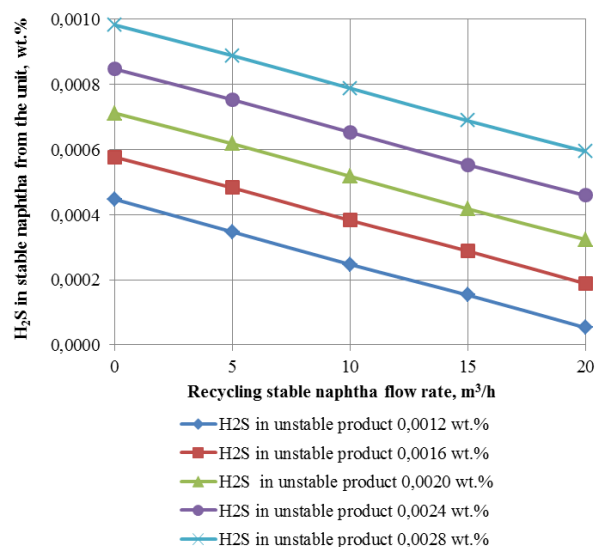


Figure 5. Impact of recycled stable naphtha flow rate on hydrogen sulphide content in product stable naphtha

As figure 5 shows, when recycled stable naphtha flow rate into the column increases from 0 to 20 m³/h, the content of hydrogen sulphide in product stable naphtha falls gradually from 0.0010 to 0.0001 wt.% depending on hydrogen sulphide content in the column feedstock.

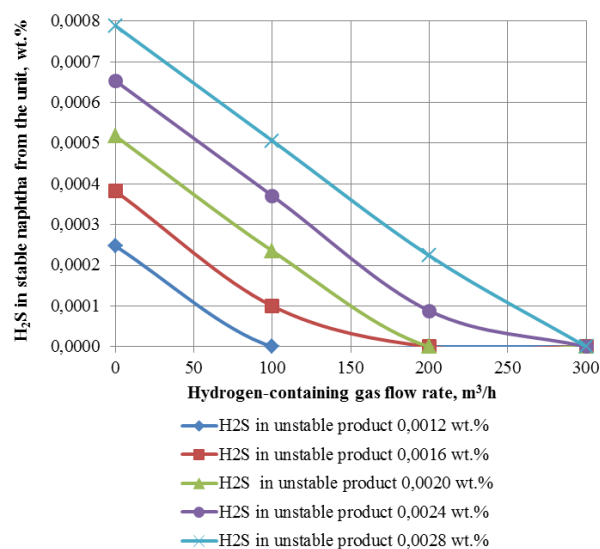


Figure 6. Impact of hydrogen containing gas flow rate on hydrogen sulphide content in product stable naphtha

As it can be seen from figure 6, increase in hydrogen-containing gas flow rate into the column from 100 to 300 m³/h causes decrease in hydrogen sulphide content in product stable naphtha from 0.0008 wt.% to complete removal depending on hydrogen sulphide content in the column feedstock.

4. Conclusion

As a result of the performed research on mass transfer intensification and hydrogen sulphide removal in stabilizer column, the dependencies of reflux and recycled naphtha flow rates on hydrogen sulphide content in product stable naphtha and its corrosiveness were established. Thus, with increase in reflux flow rate and flow rate of recycled stable naphtha into the bottom of the column, hydrogen sulphide content in product stable naphtha decreases. However, these features do not provide complete removal of hydrogen sulphide. This becomes possible by injection of hydrogen-containing gas into the column

as additional vapourizing agent, which ensures increase in partial pressure of hydrogen sulphide. The latter provides complete removal of hydrogen sulphide as a part of overhead product.

The revealed correlations made it possible to determine optimal intervals of column operating conditions. Maintenance of reflux rate in the range of 80–90 m³/h and injection of additional vapourizing agents into the column, namely recycled stable naphtha from distillation stage (in the volume of 10–22 m³/h) and hydrogen-containing gas (in the volume of 100–300 m³/h), ensure attainment of hydrogen sulphide absence in product stable naphtha. Reduction of stream corrosive activity due to suggested solutions extends service life of equipment and pipelines at industrial catalytic dewaxing unit.

References

- [1] Hinds G, Wickström L, Mingard K and Turnbull A 2013 *Corros. Sci.* Impact of surface condition on sulphide stress corrosion cracking of 316L stainless steel. Vol. **71** pp. 43–52.
- [2] Roffey P and Davies E H 2014 *Eng. Failure Anal.* The generation of corrosion under insulation and stress corrosion cracking due to sulphide stress cracking in an austenitic stainless steel hydrocarbon gas pipeline. Vol. **44** pp. 148–157.
- [3] Zheng S, Chen L, Chen C. 2013 *Eng. Failure Anal.* Failure analysis of an A333Gr6 pipeline after exposure to a hydrogen sulfide environment. Vol. **35** pp. 516–523.
- [4] Kim S J, Jung H G, Park G T, Kim K Y. 2014 *Appl. Surf. Sci.* Effect of Cu and Ni on sulfide film formation and corrosion behavior of pressure vessel steel in acid sour environment. Vol. **313** pp. 396–404.
- [5] Fellah M F. 2016 *Fuel Process. Technol.* Adsorption of hydrogen sulfide as initial step of H₂S removal: A DFT study on metal exchanged ZSM-12 clusters. Vol. **144** pp. 191–196.
- [6] Medvedeva M L 2005 *Petroleum and Gas*. Corrosion and protection of petroleum and gas processing equipment: Textbook for higher education universities of petroleum and gas profile. pp. 312.
- [7] Belinskaya N S, Ivanchina E D, Ivashkina E N, Frantsina E V and Silko G Y 2014 *Procedia Chem.* Optimal technological parameters of diesel fuel hydroisomerization unit work investigation by means of mathematical modelling method. Vol. **10** pp. 258–266.
- [8] Belinskaya N S, Ivanchina E D, Ivashkina E N and Silko G.Y. 2014 *Procedia Chem.* Effect of feed composition changing at naphtha catalytic reforming unit due to involvement of gasoline fraction obtained by diesel fuels hydrodewaxing into the processing. Vol. **10** pp. 267–270.
- [9] Belinskaya N S, Ivanchina E D, Ivashkina E N, Chuzlov V A and Faleev S A 2015 *Procedia Eng.* Mathematical modeling of the process of catalytic hydrodewaxing of atmospheric gasoil considering the interconnection of the technological scheme devices. Vol. **113** pp. 68–72.
- [10] Frantsina E V, Ivashkina E N, Ivanchina E D, Romanovskii R V, 2014 *Chem. Eng. J.* Developing of the mathematical model for controlling the operation of alkane dehydrogenation catalyst in production of linear alkyl benzene. Vol. **238** pp. 129–139.
- [11] Dolganov I M, Pisarev M O, Ivashkina E N, Dolganova I O, 2015 *Petroleum and Coal*. Modeling of liquid separators work in gas and gas condensate preparation unit in low-temperature separation technology. Vol. **57** pp. 328–335.
- [12] Dmitriev V M, Gandga T V, Dolganov I M, Pisarev M O, Dolganova I O, Ivashkina E N, 2015 *Petroleum and Coal*. Structure of network simulator for training and retraining of operators of controlled technological objects of oil and gas industry. Vol. **57** pp. 691–695.