CURRENT PROBLEMS. Standardization

STANDARDIZING AND REDUCING SULFUR CONTENT IN GASOLINES AND GASES

A. G. Akhmadullina, R. M. Akhmadullin, and S. I. Agadzhanyan

It is shown that the normative-technical documents currently in effect for liquefied gases - the feedstock for producing high-octane gasoline additive - do not allow control of total sulfur content in the gases. In view of the new sulfur content requirements for fuels, it is essential to revise without delay the normative-technical documents for liquified hydrocarbon gases in terms of the list of controllable parameters and the standards for hydrogen sulfide, mercaptan, and total sulfur content.

Key words: *liquified gases, demercaptanization, methyl-tert-butyl ether, automobile gasoline, sulfur content, heterogeneous sulfur purification catalyst.*

The tightening of requirements on the sulfur content of gasoline is elevating standards on the sulfur contents of high-octane additives used in gasoline: methyl-*tert*-butyl ether (MTBE), alkylate, and polymer benzene. The feedstock for the synthesis of these additives is the butane-butylene fraction (BBF) obtained on catalytic cracking units. The content of mercaptan sulfur is 0.01-0.02 wt. % in BBF obtained by cracking hydrotreated vacuum gas oil and 0.03-0.07 wt. % in BBF obtained by cracking vacuum gas oil that has not undergone hydrotreating.

The index "mass fraction of hydrogen sulfide and mercaptan sulfur." is monitored for BBF in accordance with existing standard TU 0272-027-00151638–99. This index is determined by the potentiometric method in accordance with GOST 22985–90. The maximum allowable value of the index is 0.015 wt. % for BBF of grade A and 0.02 wt. % for BBF of grades B and C. The index and the stringent standards just mentioned were introduced into specifications in the 1990s and took the place of the index "total sulfur content." The substitution was made based on the fact that more than 95% of the sulfur in propane and butane fractions is in the form of hydrogen sulfide and mercaptans, and during the 1990s most oil refineries were using inefficient non-recyclable alkali solutions to remove sulfur from liquified gases.
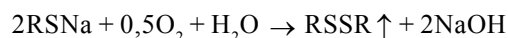
The situation today is quite different. Nearly all refineries subject liquified gases to deep demercaptanization by using recyclable alkali solutions in a process that includes two stages:

283

% extraction of mercaptans with an alkali

$$RSH + NaOH \rightarrow RSNa + H_2O$$
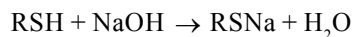
% regeneration of the alkali

$$2RSNa + 0{,}5O_2 + H_2O \rightarrow RSSR\uparrow + 2NaOH$$

Organic disulfides are formed when the mercaptan-saturated alkali solution is regenerated by its oxidation with air oxidation in the presence of a phthalocyanine catalyst (homogeneous catalysts such as Merox, VNIIUS-12, or DMD-2 or a heterogeneous catalyst such as Demer-LUVS). The disulfides have a low solubility in alkalis and good solubility in hydrocarbons. The regenerated alkali is then carefully washed with benzene to completely remove disulfides from it, since any residual disulfide that enters the extractor will be transferred from the regenerated alkali to the product being cleaned and thereby raise its overall sulfur content.

A homogenous mercaptan-oxidation catalyst dissolves in the alkali solution and circulates with it from the regenerator to the extractor and back. The presence of the catalyst and dissolved oxygen in the circulating alkali solution leads to oxidation of the mercaptans in the disulfides not only inside the regenerator but also in the pipes and the extractor. The disulfides that are formed outside the regenerator increase the overall sulfur content of the product being cleaned (BBF) [1].

In connection with the severe stiffening of the regulations on the sulfur content of gasolines and gasoline additives, it is best to regenerate mercaptan-bearing alkali solutions in the presence of a heterogeneous catalyst. The catalytically active components of the heterogeneous catalyst used in the Demer-LUVS process [2] are insoluble in alkalis and are strongly attached to the polymeric support, which keeps them from entering the circulating alkali solution. It was shown in [3] that almost no mercaptans are oxidized in alkali solutions in the absence of a catalyst.

The potentiometric method set forth by the standard TU 0272-027-0015638–99 for determining sulfur content does not make it possible to detect disulfides in BBF that are transferred from BBF to MTBE or polymer benzene and increase their sulfur content. No provision for monitoring sulfur content is included in the standards TU 38.103704–90 and TU 2435-412-05742686–98.

Similar problems are encountered in attempting to analytically monitor the sulfur content of liquified gases used as fuels by public utilities and as motor fuel. A recyclable alkali solution is also used for the demercaptanization of these gases, i.e. any disulfides that are not washed out of the alkali can end up in the gases. However, in accordance with the new regulation GOST R 52087–2003 (and the standard GOST 20448–90 that was previously in effect), only the total contents of hydrogen sulfide and mercaptan sulfur are to be analyzed in "the gases of liquified hydrocarbon fuels." These analyses are to be performed either in accordance with GOST 22985–90 or by the chromatographic method stipulated by GOST R 50802–95. Unmonitored contamination of liquified gases by disulfides can cause problems with the use of those gases in the petrochemical industry, automotive transportation, and homes. The problems are caused either by the "appearance" of a liquid residue in the fuel in the form of disulfide "oil" or by increased emissions of oxides of sulfur during combustion of the gases.

Thus, the standards currently in effect for liquified gases do not provide for objective monitoring of their quality. Given the new technologies that have been developed for purifying gases and the more exacting requirements that have been put in place for the quality of gasolines, the standards for liquified hydrocarbon

gases need to be modified as soon as possible with respect to the list of indices that are monitored and the norms in effect for the gases' contents of hydrogen sulfide and mercaptan sulfur and total sulfur content.

For example, the standard TU 0272-027-00151638–99 needs to be revised in such a way as to reduce the allowable maximum for the combined content of hydrogen sulfide and mercaptan sulfur to 5 million^{-1} and introduce a "Total sulfur content" index with a maximum limit of 10 million^{-1}. With BBF containing 14-15 wt. % isobutylene - a hydrocarbon which participates in the synthesis of MTBE and polymer benzene - the concentration of disulfide sulfur in the synthesis products becomes 6-7 times greater than in BBF and reaches ~50 million^{-1}. This level of concentration is acceptable for class-4 gasoline. The treated BBF used for alkylate production does not contain any disulfides after MTBE is separated from it and methanol is washed out of it.

The disulfides that enter MTBE and polymer benzene are not aggressive from the standpoint of corrosion. When gasoline is stored in air, the disulfides may slow its oxidation as a result of free-radical destruction of the peroxide compounds that are formed [4], i.e. the disulfides act as natural anti-oxidants [5]. In contrast to mercaptans, disulfides improve the anti-wear properties of fuels [6].

In light of the foregoing, it would not be cost-effective to rid gasolines of sulfur down to the class-5 standard, i.e. to 10 million^{-1}. Doing so would entail unjustifiably large energy and material costs for the equipment needed to remove sulfur and larger expenditures on expensive synthetic anti-oxidant and anti-wear additives for class-5 gasolines.

REFERENCES

1. V. A. Fomin, A. F. Vil'danov, A. M. Mazgarov, et al., Neftepererabotka i Neftekhimiya, No. 12, 14-15 (1987).
2. A. G. Akhmadullina, B. V. Kizhaev, G. M. Nurgalieva, et al., Ibid., No. 2, 39-41 (1994).
3. A. G. Akhmadullina, B. V. Kizaev, I. K. Khrushcheva, et al., Ibid., No. 2, 19-23 (1993).
4. K. Ingold, Usp. Khim., 3, No. 9 (1964).
5. V. A. Lyubimenko, I. N. Grishina, R. A. Gizatullin, et al., Fiz. Tekh. Tverd. Tela, No. 1, 34-35 (2008).
6. T. N. Mitusova, S. A. Loginov, E. V. Polina, et al., Ibid., No. 3, 24 (2002).