BIODIESEL FUEL AS A WASHING OIL TO IMPROVE COKE OVEN GAS QUALITY

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Recently, there have been developments on application of rapeseed-based biodiesel for cleaning coke oven gas from benzene hydrocarbons [1]. The advantage of using biodiesel in comparison with coal tar wash oil is high absorption capacity and higher boiling point, which allows to reduce the transfer of light absorbent fraction to the obtained crude benzene.

The advantage of biodiesel over other absorbents of benzene hydrocarbons is also a very narrow distillation interval.

Serious problems of coke oven gas purification are associated with the presence of naphthalene, which is in sublimated and vaporous state in coke oven gas. The presence of naphthalene worsens gas transportation, causes the appearance of deposits, which have the property of clogging gas fittings, apparatuses, communications, automatic control equipment, etc. In this connection the estimation of possibility of application of biodiesel fuel for gas washing to remove naphthalene is of special interest.

It is known that degree of coke oven gas purification from naphthalene by coal tar wash oil depends on pressure of naphthalene vapours above the oil [2]. Since the wash oil can contain from 5.0 to 16.0 % of naphthalene, the degree of purification of coke oven gas is low, as it is limited by the corresponding equilibrium concentration. Biodiesel, as a product of vegetable oil transesterification, does not contain naphthalene, which makes it a very attractive absorbent at a certain cost ratio of the absorbents under consideration.

Coal tar wash oil is a multi-component system and boils over a wide temperature range (230 to 300 °C). Biodiesel, unlike wash oil, has quite a different distillation characteristic, it is an ester, has some polarity, contains molecules with chain length from 16 to 18 atoms, the boiling points of which are close (boiling point of different types of biodiesel is 330-357 °C).

The objective of the present study was to determine the absorption capacity of biodiesel towards naphthalene. Biodiesel from sunflower oil from “Bionaphtha plant” was purchased for the study.

The absorption capacity of liquid absorbers is usually characterised by the equilibrium concentration of the absorbed substance in the liquid phase and in the vapours above the liquid at certain values of temperature and pressure. On the basis of numerous studies, it has been found that solar oil is the most optimal and available absorbent for naphthalene.

Equilibrium concentrations of naphthalene in the liquid phase and in vapours above the liquid obey Raoul's law. Raoul's law is applicable to ideal solutions and is expressed as:

$$p = p_0 \times x, \tag{1}$$

where p – partial pressure of naphthalene over the absorber solution, Pa; p_0 – pressure of saturated vapour of naphthalene over pure naphthalene, Pa; x – mole fraction of the substance in the solution.

The pressure of saturated vapour of naphthalene in different temperature ranges is described by the following equation:

$$lg\ p = A - \frac{B}{C+t} + 2{,}1238, \tag{2}$$

where p is pressure, Pa; t - temperature, °C.

The values of coefficients for naphthalene in the temperature range 0 - 80.27 ^{o}C are: A=5.8010; B=978.66; C=118.39.

In the expression of Raoul's law, p_o denotes the vapour pressure of pure naphthalene over supercooled liquid at a certain temperature. And in the above formula (2) and the given values of the coefficients, the vapour pressure is given over a solid (p_s). These values are related by the expression:

$$p_s = p_o \times N_{max}, \tag{3}$$

where N_{max} – molar fraction of naphthalene in saturated solution.

The theoretical solubility of naphthalene in methyloleate (biodiesel) was calculated using the well-known Schroeder-Le Chatelier equation [2]:

$$lnX = \frac{L_f\left(T - T_A\right)}{R\,T\,T_A} \tag{4}$$

where X – mole fraction of substance in solution A; L_f – molar heat of fusion (crystallisation) of a substance A, kJ/kg-mol; T – process temperature, К; T_A – melting point of the pure substance A, К; R – gas constant, 8.31447 kJ/kg mol K.

Experimental determination of equilibrium for the system "biodiesel – naphthalene" was carried out by the method of dynamic equilibrium [2] using chromatograph "Crystal 2000 M with software "Chromatek Analytic". The determination results were compared with the calculated values according to formulas (1)–(4) and are shown in Fig. 1.

We have experimentally checked that the solubility of naphthalene in biodiesel is 30 g/100 g at 25 °C, which exceeds the theoretical solubility of naphthalene in methyloleate by 1.9 times according to Le Chatelier's formula (4). This, apparently, explains the deviations of experimental data from Raoul's law.

The calculated data on the absorption capacity of biodiesel in comparison with other absorbers are given in Table 1.

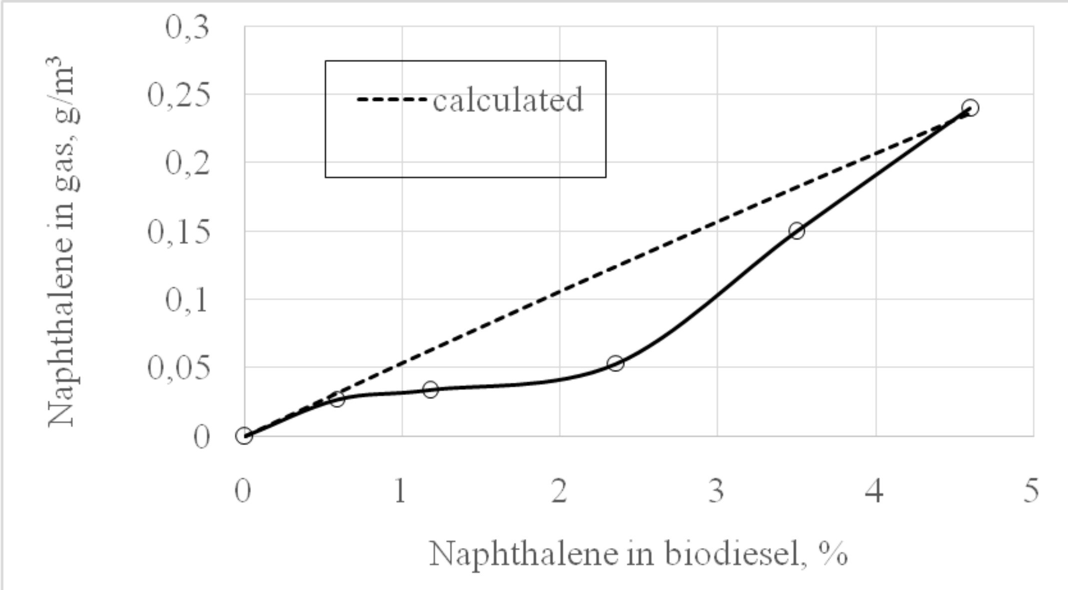

Figure 1 – Experimental and calculated values of equilibrium concentrations of naphthalene over biodiesel at 25 °C.

Table 1. – Comparative characterisation of different naphthalene absorbents

Mass fraction of naphthalene in solution, %	Equilibrium concentration of naphthalene in gas at 25 0C, g/m^3			
	Solar oil	Biodiesel	Anthracene oil	Tetralin oil
1.0	0.04	0.045	0.02	0.015
2.0	0.08	0.090	0.05	0.025

Conclusions

As a result of the performed work, it was experimentally established that the absorption capacity of biodiesel fuel in relation to naphthalene is comparable to that of solar oil, but unlike the latter, it does not form sludge when interacting with coke oven gas tars. Such combination of absorber properties allows to recommend it for additional treatment of coke oven gas from naphthalene.

References

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