INTRODUCTION

The increasingly stringent regulations on the content of poisons in the exhaust fumes of automobile engines have naturally led to the introduction of new specifications for motor fuels. In Europe, diesel fuel with a sulfur content no greater than 50 ppm (Euro-4) was used beginning from 2005. On January 1, 2009, the sulfur content was reduced to 10 ppm (Euro-5). In Russia, the Euro-4 standard was introduced on January 1, 2015, to be followed by Euro-5 exactly one year later. The use of state-of-the-art catalysts for the deep hydrotreatment of diesel fractions and vacuum gas oil, the feedstock for catalytic cracking and hydrocracking, therefore continues at Russian refineries [1, 2].

To develop new catalytic systems and predict the behavior of sulfide catalysts in the hydrotreatment of petroleum distillates, the catalytic properties of granular catalyst are studied using three-phase flow reactors under conditions identical to those of operating industrial hydrotreatment units. However, obtaining reliable and reproducible results on granular catalysts in three-phase reactors is complicated by mass and heat transfer processes, and by phenomena such as the incomplete wetting of the catalyst, the wall effect, and the back-mixing of liquids. Laboratory facilities and analysis techniques are described, and results obtained at different laboratories in studying catalysts for the deep hydrotreatment of diesel fractions are compared.

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In this work, we consider current approaches to testing the granular catalysts of petroleum distillate hydrotreatment in the laboratory and describe the equipment used to study the catalytic properties of hydrotreatment and hydrocracking catalysts.
catalyst interfaces) can considerably distort the experimental results.

The hydrotreatment of catalysts studied over a period of several years at pilot plants with catalyst volumes of around 10 liters. This entailed substantial capital outlays and high operating costs. However, the continued desire to reduce the cost of research and improve its safety stimulated the development of approaches that allow us to reduce reactor size and catalyst loading considerably [3, 4].

The smallest possible size of a reactor is determined by the possibility of ignoring the wall effect and its associated radial nonuniformity of the reaction mixture’s flow rate, along with external diffusion and the effects diffusion caused by the uneven distribution of the catalyst granules in the reactor. Based on the criteria for a hydrodynamic flow reactor, the diameter of tubular reaction zone should thus be at least 8–10 times greater than that of the catalyst granules’ effective diameters, while the length of the reaction zone should be at least 40–50 times greater [5–8]. If we assume that the effective diameter of a commercial catalyst pellet is approximately 1.5 mm, the minimum inner diameter of the laboratory reactor would be around 12 mm, and the reaction zone length (the catalyst bed height) would be at least 60 mm. Based on the values for the reactor diameter and height of the catalyst bed, we can estimate the minimum catalyst loading to avoid the influence of external diffusion on the test results. For a reactor 12 mm in diameter, the minimum amount of catalyst is thus around 7.5 mL.

Unlike industrial reactors, a very low linear velocity of the liquid–gas mixture is typical of laboratory reactors. Consequently, individual phases can be separated and stable gas bubbles can form, hindering the simultaneous access of the hydrogen and the liquid phase to the catalyst’s surface. This results in incomplete wetting of the catalyst and an inhomogeneous flow rate in the areas of such bubbles. To eliminate these effects and maintain high dispersion of the gas phase, the catalyst pellets are diluted with fine particles of an inert diluent (typically silicon carbide), whose surface is thoroughly wetted with diesel fraction. As a result, the wettability and the uniformity of the liquid–gas distribution in the catalyst bed are improved and the wall effect is minimized. In the case of such a loading, hydrodynamic reactor properties are determined by the packing of fine particles, while catalytic properties are determined by catalyst particles with the same the shape and size as in industry [9].

The method of diluting the catalyst bed with inert fine particles of a nonporous material is widely used for catalyst testing in the hydrotreatment of petroleum distillates. It allows us to achieve tests results that are reproducible in reactors of different sizes. In [3], the same results were obtained during hydrotreatment catalyst testing in a laboratory reactor (catalyst loading, 9.35 mL) as when this catalyst was used in a commercial reactor of 122 m$^3$ in volume.

There are a number of works devoted to studying the influence of the diluent particle size (or the ratio of the particle sizes of the diluent and catalyst), the direction of the gas and liquid flows (top down or bottom up), the feed space velocity, and the hydrogen/feedstock ratio on the test results for hydrotreatment catalysts in laboratory scale reactors [3, 4, 9–12].

Comparing the upstream and downstream operating modes of a laboratory reactor with a diameter of 14 mm, the authors of [10] have come to the conclusion that 1 : 1 dilution of the catalyst with an inert material allows complete wetting of the catalyst, avoiding axial heterogeneity and feed bypass. In [9], it was shown that the downstream mode is preferred for gas phase supply controlled reactions, and the upstream mode is preferred for liquid phase supply controlled reactions. It was found that when a catalyst bed is diluted with an inert diluent, the difference between the results obtained in the different modes is negligible. The authors developed a procedure for catalyst loading that ensured high reproducibility of these results: the optimum size of particles of an inert diluent should be about 1/10 that of the catalyst particles [11].

Using a diluent with a particle size of 0.77 mm and low flow rates of the feedstock, higher rates of conver-

<table>
<thead>
<tr>
<th>Parameter</th>
<th>industrial</th>
<th>pilot</th>
<th>laboratory</th>
<th>microreactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst bed length, cm</td>
<td>2000</td>
<td>800</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Reactor diameter, cm</td>
<td>250</td>
<td>4</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Catalyst volume, L</td>
<td>100000</td>
<td>10</td>
<td>0.15</td>
<td>0.008</td>
</tr>
<tr>
<td>Ratio of reactor diameter to catalyst diameter†</td>
<td>1667</td>
<td>27</td>
<td>13</td>
<td>7</td>
</tr>
<tr>
<td>Ratio of catalyst bed length to catalyst diameter†</td>
<td>13333</td>
<td>5333</td>
<td>333</td>
<td>66</td>
</tr>
<tr>
<td>Liquid flow rate, cm/s§</td>
<td>0.55</td>
<td>0.2</td>
<td>0.015</td>
<td>0.003</td>
</tr>
</tbody>
</table>

* Catalyst diameter, 15 cm.
** Volume rate, 1 h$^-$

**Table 1. Comparison of industrial and laboratory reactors**

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