Adsorptive Biogas Purification

Subjects: Energy & Fuels

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Siloxanes are among the most technologically troublesome trace compounds present in biogas. As a result of their combustion, hard-to-remove sediments are formed, blocking biogas energy processing devices and reducing the efficiency of biogas plants. This entry can help to choose the optimal technology for the adsorptive removal of volatile methylsiloxanes (VMSs) from biogas and to identify adsorbents worth further development.

Both the already implemented methods of adsorptive VMSs removal from landfill and sewage gases—e.g. using activated carbon and silica gel—and the ones being under development—e.g. using polymer resins—are presented, and their advantages and drawbacks are analyzed. The methods of obtaining adsorbents and the parameters of adsorption processes are discussed, and possible ways of regenerating spent adsorbents are evaluated.

Especially promising adsorbents seem to be some zeolites—which can also be used for biogas desulfurization—and adsorbents based on polymer resins, as being particularly active towards VMSs and most amenable to multiple regeneration.

biogas treatment   volatile methylsiloxanes   adsorbents

1. Adsorption of VMSs Using Activated Carbon

Activated carbon is formed in the processes of carbonization and thermal or chemical-thermal activation of such organic raw materials as fossil coals, wood and various types of organic waste. During these processes the organic matter is partially decomposed, and volatiles are removed, whereby the activated carbon acquires a proper porous structure. Carbonization is conducted at a temperature of 600–800 °C. Then the carbonizate is subjected to physical activation, i.e., further thermal treatment with steam or CO_2 (400–500 °C) to eliminate the remaining volatiles, or to partial gasification at a temperature of 800–1000 °C. The alternative is chemical activation, i.e., roasting (500–900 °C) with the addition of zinc chloride, potassium sulfide, phosphoric acid or other chemicals[1]. All these processes lead to the formation of an extremely extensive internal structure consisting of a wide spectrum of micropores and mesopores. As a result, a universal adsorbent with the largest specific surface area—which can exceed 2000 m^2/g—among all the known adsorbents is produced. Small activated carbon rolls with a diameter of about 1–2 mm and a length of up to 4 mm are most often used in gas cleaning processes. Activated carbon fibers are used less often, but they can be more effective in removing octamethylcyclotetrasiloxane (D4) than granular activated carbon[2][3]. The feature that particularly predisposes activated carbon to VMSs removal from biogas is its non-polar structure[4] promoting the adsorption of non-polar or weakly polar VMSs. Larger pore volumes, more suitable for the size of VMSs molecules, are obtained using chemical activation with H_3PO_4[5]. Generally, many

researchers indicate that adsorbent pores with a diameter of 1.7–6.0 nm are most suitable for the adsorption of VMSs whose molecule diameter is about 1 nm.

Depending on the method of activation (and/or impregnation), activated carbon can have an acidic or basic character. According to Gong et al.[6], activated carbon activity towards VMSs increases with the increasing pH of the bed. However, alkaline impregnation, which can be used for H_2S removal, can reduce the adsorbent's active surface area and pore volume, which, in turn, can reduce its capacity to absorb VMSs[7].

The large diversity of activated carbon's pores in comparison with other adsorbents is, unfortunately, also its disadvantage, being the main cause of its low selectivity. Besides the sulfur and chlorine compounds mentioned above, activated carbon has a high affinity for other VOCs, water steam and hydrocarbons—CH_4 adsorption on activated carbon is greater than on silica gel and molecular sieve[1]. The presence of the above compounds in biogas, competing for a place in activated carbon's micro- and mesopores, reduces its capacity to adsorb VMSs and directly affects the operating costs.

Activated carbon shows greater activity towards cyclic VMSs, which is connected with the changes they undergo on its surface and the displacement of the previously adsorbed lighter linear VMSs—e.g., hexamethyldisiloxane (L2) and octamethyltrisiloxane (L3)—by heavier and less volatile cyclic VMSs—e.g., D4 and decamethylcyclopentasiloxane (D5)—or by other high-molecular aromatic VOCs and water vapor[8]. A way to reduce the above disadvantages is biogas pretreatment, consisting in condensation drying—usually up to RH < 50%—during which interfering impurities and some VMSs are partly removed with the condensate.

A more serious disadvantage of activated carbon in the removal of VMSs is their transformation, consisting in the polymerization of cyclic VMSs into less volatile, heavier and hardly desorbable polydimethylsiloxanes[9] which block the adsorbent's pores and prevent its effective thermal regeneration. This process is more intense on wood-based carbons activated with phosphoric acid than with water steam[10]. Chemical regeneration through the oxidation of the adsorbed VMSs (with O_3, H_2O_2 or iron salts) also fails because the final reaction product is SiO_2 which blocks pores[10][11].

2. Adsorption of VMSs Using Silica Gel

Silica gel is obtained by polymerizing silicic acid with H_2SO_4 or HCl to an amorphous gel having the molecular formula $(SiO_2) \cdot nH_2O$. This adsorbent is typically used in the form of beads with a diameter of 1–5 mm. It is characterized by high porosity and a polar structure. The latter feature endows silica gel with a special affinity for water, making it one of the most effective desiccants. Therefore, deep drying—below 10% RH—is required in order to effectively remove VMSs from biogas[12]. In comparison with activated carbon, silica gel is characterized by a smaller specific surface area (350–700 m^2/g) and larger pore sizes, with the predominance of mesopores, which is beneficial for VMSs adsorption. Most researchers—e.g. [13][14][15]—indicate silica gel's higher selectivity and affinity for VMSs (provided that the biogas is properly dried), especially in the case of lighter chain forms, such as L2. Since silica gel has a lower capacity to adsorb sulfur compounds, it can be more useful for the purification of LFG

which usually contains less H_2S. Most researchers also indicate that silica gel is more amenable to regeneration. According to Yang[1], since silica gel's adsorption forces are weaker, it should be easier to thermally regenerate than activated carbon.

In recent years, besides the use of conventional silica gel, attempts have been made to modify silica gel in order to improve its adsorption capacity and regenerability. By treating silica gel with acetic anhydride Liu et al.[16] obtained an interesting hydrophobic silica gel modification whose adsorption capacity, regardless of biogas humidity, amounted to 304 g/kg for L2 and to 916 g/kg for D4—much more than in the case of activated carbons. Its regeneration was trouble-free at a relatively low temperature of 110 °C.

3. Adsorption of VMSs Using Zeolites

Natural zeolites comprise hydrated alkali metal aluminosilicate minerals with a crystalline structure, such as modernite, chabasite, clinoptilolite, silicalite and others. Their activation is based on thermal treatment, as a result of which they lose water and acquire an ordered internal structure with uniform pore sizes (hence the name "molecular sieves"), whereby, as opposed to active carbons, they become selective adsorbents. Zeolites are also made synthetically—e.g., 3A, 4A, 5A, 10X, 13X, ZSM-5. Depending on the ratio of silicon to aluminum atoms, they can be hydrophobic (Si/Al>10) or hydrophilic (Si/Al < 1.5). Hydrophobic zeolites are more useful for removing nonpolar and weakly polar compounds, including VMSs. For example, zeolite such as ZSM-5 with a high Si/Al ratio (200)[17] can be used simultaneously for CO_2 and H_2O removal in the biogas upgrading process and for the removal of VMSs and H_2S.

Zeolites are also characterized by high mechanical and thermal resistance (up to 600 °C). In comparison with activated carbon and silica gel, they have a comparable or slightly smaller specific surface area (370–910 m^2/g). Owing to the uniform size of their pores they can work more efficiently if they are selected with regard to the composition of the particular biogas. Unlike silica gel, they can simultaneously remove H_2S—thanks to their alkaline nature—and their affinity for CH_4 is several times lower than for activated carbon[1].

The usefulness of zeolites for removing VMSs from biogas has been confirmed by numerous studies, e.g.,[8][18][19]. Owing to their high thermal resistance they are also suitable for repeated thermal regeneration[2].

4. Adsorption of VMSs Using Activated Alumina

As recent research has shown one of the effective VMSs adsorbents is activated alumina[20][21], which is obtained by calcining hydrated aluminum hydroxide in the presence of oxygen at a temperature of about 400 °C. The resulting porous, crystalline structure is characterized by a distinct predominance of mesopores (3–7 nm) and a specific surface area of 200–250 m^2/g. Further roasting (up to 800 °C) leads to an amorphous form with a larger specific surface area amounting to 300–400 m^2/g.

The synthetic adsorbent based on alumina (Al120-8h) developed by Zhong et al.[20], due to its larger specific surface area and porosity, proved to be a better D4 adsorbent than the commercial activated alumina. Its advantage is the possibility of effective regeneration with no apparent VMSs polymerization effect. It should be noted, however, that due to its relatively large pores, activated alumina is better suited for cyclic VMSs.

5. Adsorption of VMSs Using Polymer Resins

Polymer adsorbents are obtained by polymerizing monomers, i.e., styrene cross-linked with divinylbenzene (DVB) and acrylates, in the presence of an organic solvent. Popular DVB-based resins include XAD-2 and XAD-4 hydrophobic polymers, whereas the ones based on acrylic ester (e.g., XAD-7) are hydrophilic[1]. Especially the former—as opposed to activated carbons and silica gel—are well suited for the purification of moist biogas, the more so because they are non-polar. Unfortunately, their thermal strength is low (<200 °C), which can potentially hinder the thermal desorption of some VMSs. Owing to their dense cross-linking they are relatively stiff and mechanically strong. This also contributes to their high porosity and specific surface area (up to 1000 m^2/g). In addition to the traditional polymer adsorbents mentioned above, in recent years new resins for VMSs adsorption have been synthesized. A particularly interesting series of adsorbents (PDVB-VI) based on the copolymerization of divinylbenzene with 1-vinylimidazole have been developed by Jafari et al.[22]. These adsorbents have an extremely large pore volume and specific surface area, whereby their adsorption capacity for VMSs is very high—in the order of 2000 g/kg. In addition, they can be effectively regenerated at a relatively low temperature (~100 °C), which indicates no polymerization of VMSs on their surface. The ease of regeneration of polymer adsorbents has also been confirmed by other authors[23][24]. Despite such advantageous characteristics, these adsorbents are not commercially used for gas purification due to their high price.

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