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Cyclonic gas stripping deoiling and gas flow acceleration classification for the resource utilization of spent catalysts in residue hydrotreating process

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ABSTRACT

The resource utilization of spent catalysts is one of the keys to enabling ebullated bed hydrotreating technology to be environmentally friendly, resource-saving and process sustainable. Spent residue hydrotreating catalysts contain a large amount of oil and highly active catalysts, if cannot be efficiently recycled will lead to waste of resources and huge catalyst consumption. In this study, the novel cyclonic gas stripping was first developed to spent catalysts deoiling, in which the removal of oil filled in the catalyst nanopores was enhanced by particle high speed self-rotation. Meanwhile, gas flow acceleration classification was developed for catalyst activity classification according to the particle density differences. This technology was successfully applied to the SINOPEC's first set of ebullated bed residue hydrotreating industrial demonstration unit, the total oil content of spent catalysts can reduce to 1.7% from 31.8%, with the deoiling efficiency reaching 96.7%. Moreover, 30% of the catalysts after deoiling were classified as highly active catalysts with lower particle density and higher pore volume. The successful implementation of this technology can reduce 25% of fresh catalyst consumption and 52% of hazardous waste discharge in residue hydrotreating process. This technique also can be extended to the resource utilization of spent catalysts in other petrochemical production.

1. Introduction

Currently, catalysts are indispensable in more than 90% of the industrial production process, and 35% of the global GDP depends on catalytic action (Armor, 2011; Cole-Hamilton and Tooze, 2006). The consumption of industrial catalysts is up to 800,000 tons/year in 2012, including 750,000 tons/year in oil refining and chemical industries (Li et al., 2016). According to a new report published by Allied Market Research in 2017, the catalysts market is expected to reach $40 billion by 2022 up from $28.6 billion in 2015, with a compound annual growth rate of 4.8% from 2016 to 2022. The catalyst deactivation and passivation occurs during the whole reaction process due to coke and heavy metals deposition in catalyst nanopores (Akcil et al., 2015; Dufresne, 2007; He et al., 2010; Liu et al., 2016; Novaes et al., 2017; Rana et al., 2014). The huge consumption of catalysts inevitably discharge a large number of spent catalysts containing toxic substances, has become a global problem in the petrochemical industry (Chiranjeevi et al., 2016; Furimsky, 1996; Nahm et al., 2012; Nunes and Costa, 2017; Rana et al., 2014).

First, spent catalysts always absorb a large number of petroleum contaminants, such as alkanes, aromatic hydrocarbons, colloids, and asphalts (Marafi and Furimsky, 2017; Marafi and Stanislaus, 2003, 2008). Most of the contaminants were absorbed in the particle surface and nanopores (Ayen and Swanstrom, 1992; Li et al., 2016; Rana et al., 2014). Directly landfill or incineration not only result in waste of resources, but also possibly cause pollutants to enter the atmosphere, water, and soil environments (Yang et al.,

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2011). Given the environmental risks from spent catalyst, environmental authorities around the world have formulated strict environmental protection laws and regulations. The United States Environmental Protection Agency lists spent catalysts as hazardous waste that pose a substantial or potential hazard to human health and environment (Marafi et al., 2008). Furthermore, the developed pore structure of catalysts resulting in an extremely high oil content (20–60 wt%) of spent catalysts, the oil recovery is particularly important in the age of energy growing shortage (Li et al., 2016).

Second, because of the flow regime of full back mixing in ebullated bed reactor (Aldalama and Stanislaus, 2006; McKnight et al., 2003; Pjontek et al., 2015), which cause the mixing of highly active and lowly active catalysts in the discharged catalysts (Aldalama and Stanislaus, 2006; Angeles et al., 2014). Taking the SINOPEC's first set of ebullated bed residual oil hydrotreating demonstration unit as an example, the catalysts that retain 80% initial catalyst activity cover nearly 50% of the total discharged catalysts. If these highly active catalysts are directly discarded with waste catalysts, it will not only create large emissions of hazardous waste, but also result in huge waste of catalyst resources and high consumption of fresh catalysts.

Therefore, efficient separation and recovery of oil and highly active catalysts from spent catalysts are keys to utilization of spent catalysts in residue hydrotreating process (Molnár and Papp, 2017). Currently, the treatment of spent catalysts in petrochemical industry is mainly rest on the oil removal and recycling; the main methods are high temperature treatment and solvent extraction (Ji and Guo, 2010; Lin et al., 2017; Menoufy and Ahmed, 2008; Merino and Bucala, 2007; Zubaidy and Abouelnasr, 2010). High temperature treatment is conducted to distill the oil and recovery oil by condensation, easy operation but high energy consumption and low removal efficiency for oil filled in the nanopores of catalysts (Gilot et al., 1997; Kante et al., 2008; Merino and Bucala, 2007). The oil removal efficiency of solvent extraction is usually high, but the recycling of extracting agents is difficult; most extraction treatment procedures still stay in the experimental stage (Hu et al., 2013; Liu et al., 2009).

Research on the classification of catalysts discharged from ebullated bed residue hydrotreating has not been reported. Catalysts deactivate is due to coke and metals deposition in the developed nanopores, as a result, their porosity decreases and particle density increases gradually (Akcil et al., 2015; Jeon et al., 2011; Novaes et al., 2017; Rana et al., 2014). Therefore, the activity of catalysts is positively correlated to the particle density, the smaller the catalyst particle density, the higher the catalytic activity. Hence, the particle density difference provide favorable conditions for the classification and reuse of highly active catalysts (Duan et al., 2014).

In this study, the technology of cyclonic gas stripping deoiling was first developed based on catalyst high speed self-rotation in gas cyclone (Huang et al., 2017a, 2017b; Li et al., 2016), which greatly enhanced the centrifugal removal and mechanical stripping of oil filled in the catalyst nanopores. After oil removal, the density difference of highly and lowly active catalyst particles was utilized to develop the technology of gas flow acceleration classification, and the highly active particles are classified and reused. Thus achieving the resource utilization of spent catalysts and enabling ebullated bed hydrotreating technology to be environmentally friendly, resource-saving and process sustainable.

2. Material and methods

2.1. Cyclonic gas stripping deoiling and gas flow acceleration classification

In our previous studies on cyclone and hydrocyclone, we have found that particles not only revolve around the axis of the equipment, but also rotate around its own center, named self-rotation (Huang et al., 2017a, 2017b). More importantly, the speed of self-rotation and the centrifugal force generated by particle self-rotation are much larger than those of revolution (Huang et al., 2017a, 2017b; Li et al., 2016). The speed rate of particle self-rotation can be up to 2000–6000 rad/s in the adopted cyclone with a body diameter of 75 mm. The high speed self-rotation creates a good condition for the centrifugal removal and mechanical stripping of oil filled in the catalyst nanopores. The technical principle of cyclonic gas stripping deoiling and gas flow acceleration classification is shown in Fig. 1. The oilly spent catalysts were transported into the gas stripping cyclone by high temperature gas. Under the combined action of high temperature gas and high speed self-rotation of particles, the oil was separated from the surface and nanopores of catalysts, and discharged with gas flow from the cyclone overflow. The oil can be recovered and reused by condensing the gaseous phase. After deoiling, the dry catalysts were discharged from the underflow and then were transported into gas flow acceleration classifier.

The different deposition of coke and metals in nanopores lead to the different activities of deoiled catalysts, which directly reflect in different particle densities. Researches show that particles with different densities have different acceleration characteristics in gas flow (Duan et al., 2009; Everett and Jeffrey Peirce, 1990; Jackson et al., 1988). In still gas flow, two particles with different densities and diameter but same terminal settling velocities (gas flow with a constant speed cannot achieve classification), while they were free falling at the same time, although the final velocity was the same, the downward acceleration of particle with higher density is larger than that of particle with lower density in the first 0.2 s (Jackson et al., 1988). Different accelerations of particles with different densities in gas flow make density-dominated classification possible. In the gas flow acceleration classification, with the application of sine and cosine wave-shaped pulse gas flow in the vertical classifier, the acceleration and velocity of particles is controlled by the acceleration and deceleration of gas flow. By controlling the gas flow, the upward velocity of particles with lower density in a single cycle can always be larger than that of particles with higher density. The movement of particles is affected by the “new fluid” in each pulsation cycle, so that the differences in acceleration characteristics of particles in the pulse gas flow are fully reflected and enlarged. The upward displacement of highly active catalysts (light) is larger than downward displacement in every pulsation cycle, so the total displacement is upward and these particles move towards the top of the classifier; conversely, the lowly active catalysts (heavy) move towards the bottom of the classifier. Therefore, the efficient classification of highly active catalyst particles is achieved.

2.2. Experimental setup and process

The catalyst treatment flow diagram is shown in Fig. 2(a), and the three-dimensional installation diagram and device photo in Jinling Petrochemical Corporation (SINOPEC) with a capacity of 24 kg/h are shown in Fig. 2(b) and (c). The sine and cosine wave-shaped pulse nitrogen gas flow (frequency 2 Hz) was created by blower and pulse gas flow generator. The nitrogen gas is subsequently heated to the required experimental temperature in a gas heater. The oily catalysts are added by a screw feeder and transported by the high-temperature gas to enter the gas stripping cyclone for deoiling. The deoiled dry catalyst particles slide into the gas flow acceleration classifier for the activity classification. The lowly active catalysts were direct discharged from the bottom outlet to the storage tank; the highly active catalysts were