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Separation-and-Recovery Technology for Organic Waste Liquid with a High Concentration of Inorganic Particles

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ABSTRACT

The environmentally friendly and resourceful utilization of organic waste liquid is one of the frontiers of environmental engineering. With the increasing demand for chemicals, the problem of organic waste liquid with a high concentration of inorganic pollutants in the processing of petroleum, coal, and natural gas is becoming more serious. In this study, the high-speed self-rotation and flipping of particles in a three-dimensional cyclonic turbulent field was examined using a synchronous high-speed camera technique; the self-rotation speed was found to reach 2000–6000 rad·s^{-1}. Based on these findings, a cyclonic gas-stripping method for the removal of organic matter from the pores of particles was invented. A technological process was developed to recover organic matter from waste liquid by cyclonic gas stripping and classifying inorganic particles by means of airflow acceleration classification. A demonstration device was built in Sinopec's first ebullated-bed hydro-treatment unit for residual oil. Compared with the T-STAR fixed-bed gas-stripping technology designed in the United States, the maximum liquid-removal efficiency of the catalyst particles in this new process is 44.9% greater at the same temperature, and the time required to realize 95% liquid-removal efficiency is decreased from 1956.5 to 8.4 s. In addition, we achieved the classification and reuse of the catalyst particles contained in waste liquid according to their activity. A proposal to use this new technology was put forward regarding the control of organic waste liquid and the classification recovery of inorganic particles in an ebullated-bed hydro-treatment process for residual oil with a processing capacity of 2×10^6 t·a^{-1}. It is estimated that the use of this new technology will lead to the recovery of 3100 t·a^{-1} of diesel fuel and 647 t·a^{-1} of high-activity catalyst; in addition, it will reduce the consumption of fresh catalyst by 518 t·a^{-1}. The direct economic benefits of this process will be as high as 37.28 million CNY per year.

1. Introduction

Given the current rates of industrialization and urbanization, the amount of organic waste liquid with a high concentration of inorganic particles being produced in the processing of petroleum, coal, and natural gas is increasing daily. This kind of waste liquid is involved in almost every part of the petrochemical industry [1–3], including the following processes:

(1) **Crude oil extraction, storage, and transportation** [4]. Organic waste liquid with a high sludge content accounts for 0.5%–1% of crude oil production; the annual output of oily sludge in the petroleum exploration industry alone exceeds 1×10^6 t.

(2) **Oil refining and chemical production** [5–7]. More than 90% of industrial production processes cannot proceed without catalysts, the use of which produces a large amount of organic waste liquid containing catalysts. The annual output of inorganic pollutants, including spent catalysts, in the emission of organic waste liquid from China's petroleum and chemical industry reached 1.127×10^7 t in 2016 and accounted for 41.5% of all industrial emissions in that year.

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(3) **Sewage treatment in the petroleum and chemical industries** [8–10]. The organic waste liquid in these processes mainly comes from oil-separation tanks, flotation cells in joint station sewage treatment plants, and joint stations; it includes sludge containing organic waste liquid, residual activated sludge, and so on. High-concentration organic waste liquid not only has a wide range of sources, complex components, high chromaticity, and heavy odor; it also contains a large number of toxic and harmful substances [11,12], thus posing a severe threat to our environment and ecology. It is difficult to use general wastewater treatment methods to meet the economic and technical requirements of purification treatment; therefore, the question of how to effectively deal with high-concentration organic waste liquid has become the focus of attention all over the world. In addition, the environmentally friendly and resourceful utilization of organic waste liquid with a high calorific value has become a technical problem in the environmental protection industry that urgently requires a solution.

The petroleum and chemical industries are China's foundational industries. As global oil prices rise, the quality of crude oil worsens, environmental laws and regulations become increasingly stringent, and the demand for light clean fuels grows, the deep processing of crude oil and cleaner technology for fuel production will rapidly be developed. The organic waste liquid that is produced by petroleum and chemical engineering processes has the characteristics of a conventional waste liquid, but contains a large number of inorganic particles such as porous catalysts [13,14]. Due to their porous structure, inorganic particles adsorb large amounts of organic waste liquid, which is a typical environmental pollutant and which is difficult to remove efficiently [15,16]. Therefore, the treatment of organic waste liquid with a high concentration of inorganic particles is difficult. The environmentally friendly, energy-saving, and efficient treatment of inorganic particles is the key to this technology.

At present, methods of treating the inorganic particles in organic waste liquid mainly include solvent extraction, heating distillation, direct landfill, and incineration. However, the solvent-extraction process is costly, and it is difficult to achieve solvent recovery and recycling; as a result, most extraction processing methods are still in the laboratory research stage [17]. Heating distillation requires a higher treatment temperature and high energy consumption, but results in a low removal efficiency for organic matter in the catalyst micro pores [18,19]. Direct landfill wastes a great deal of land resources, and pollutes the soil and water [20]. Incineration is not an effective use for the energy of petroleum pollutants in organic waste liquid; in addition, since inorganic particles often adsorb a large number of sulfur and heavy metal components, these components are carried into the atmosphere by tail gas during burning or calcination, resulting in secondary pollution [21]. In other words, the results of solvent extraction and heating distillation are inadequate but carry very high processing costs, whereas direct landfill and incineration are the least economical approaches and lead to secondary pollution. Thus, there is no highly efficient, energy-saving, environmentally friendly treatment method for inorganic particles in industrial organic waste.

In petroleum and chemical engineering processes, the inorganic particles found in organic waste liquid are mainly catalysts. The amount of carbon deposited on the catalysts and heavy metal components in the catalyst pores varies due to the catalysts' differing residence times in the reactor. Thus, particles have different porosities and activities [13,22–24]. As a result, spent catalyst waste contains a large number of high-activity catalysts that are discharged along with the spent catalysts. This causes a great deal of solid waste and a high processing cost, and is a great waste of catalyst resources.

Therefore, the efficient separation of organic waste liquid with a high concentration of inorganic particles, and the classification and recovery of inorganic particles, are the keys to achieving environmentally friendly and resourceful treatment of organic waste liquid. This study developed a cyclonic gas-stripping method based on the high-speed self-rotation and flipping of particles in a gas cyclonic flow field. This process strengthens the removal of the liquid phase in the micro pores of inorganic particles and allows the efficient separation of organic waste liquid and inorganic particles to be achieved. Based on the mechanism of airflow acceleration classification [25–27], inorganic particles in the waste liquid are then graded according to the pore volume. Inorganic particles with high porosity are selectively reused in order to reduce material consumption and the discharge of hazardous waste. A demonstration device with a rated processing capacity of 24 $\mathrm{kg{\cdot}h^{-1}}$ was built in Sinopec's first ebullated-bed hydro-treatment unit for residual oil. Based on the research results of this demonstration unit, a technical proposal was put forward to use this process to control organic waste liquid and to recover and utilize inorganic particles in the $2 \times 10^6\ \mathrm{t{\cdot}a^{-1}}$ ebullated-bed hydro-treatment process for residual oil.

2. The revolution, self-rotation, and flipping of particles in a gas cyclonic flow field

In a cyclonic shear flow field, inorganic particles are subjected to centrifugal, drag, and buoyancy forces that cause the macroscopic migration of particles. They are also subjected to unbalanced shear stress, which causes the self-rotation and flipping of particles. The revolution, self-rotation, and flipping of dispersed-phase particles in a cyclonic flow field are very important for studying the separation, desorption, absorption, trapping, and extraction process inside a cyclone [28,29]. This study used a high-speed camera system (Fig. 1) to observe the movement of inorganic particles in a dispersed phase in a gas cyclonic flow field, in order to provide theoretical support for the high-speed self-rotation and flipping of inorganic particles and thus strengthen the concept behind the proposed technology to remove organic waste liquid from the surfaces and pores of particles. The test system is composed of three parts: a high-speed digital camera, a light source, and a computer. The motion of the particles was obtained using image analysis software. The high-speed digital camera was produced by Photron, Japan (FASTCAM SA-X2); it has a maximum shooting speed of 216 000 frames per second (fps), and a maximum image size of 1024 × 1024 pixels.

The structural parameters of the cyclonic flow field and the layout of the experimental setup are shown in Fig. 2. In order to investigate the movement of particles in the cylindrical and conical sections of the cyclone, the cyclone was divided into two sections—$Z1$ and $Z2$—at the interface of the column and cone. The height of each section was 90 mm, and each section was investigated separately. The particles chosen for observation were carbon sticks with a diameter (d_r) of 0.5 mm and a length-diameter ratio of 2.14.

Fig. 3 shows the motion of the particles that was obtained by synthesizing high-speed photographs with a frequency (f) of 10 000 fps. Since a particle's displacement in two adjacent photographs is less than its diameter, in order to clearly reflect the motion of the particles, the time between two synthetic photos (Δt) is 0.4 ms. It can be seen from the particle motion images that there are three main forms of motion of particles in a cyclonic flow field: self-rotation, flipping, and revolution. Particle self-rotation (ω_m) is defined as the self-rotation of particles around their long axis; it can be identified by the gap at both ends of the particle. Particle flipping (ω_n) is defined as the self-rotation of particles around

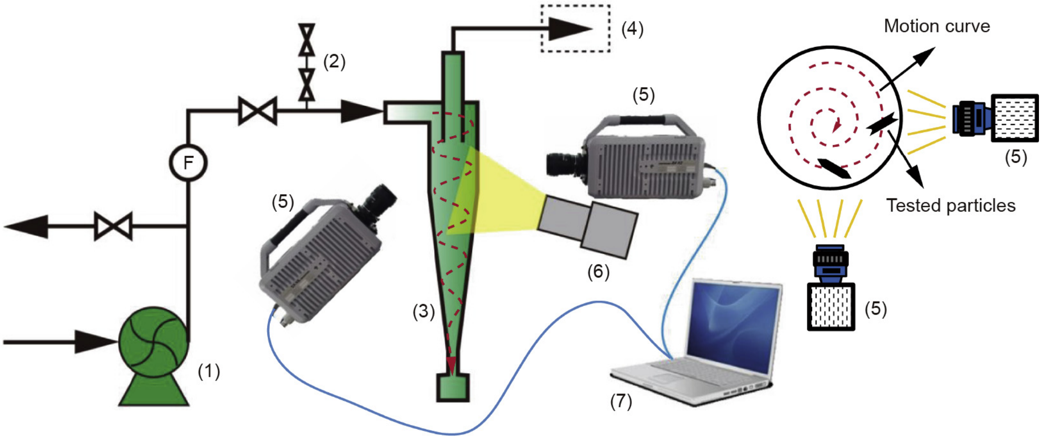


Fig. 1. A testing system for the synchronous high-speed camera measurement of the particle movement in a cyclonic flow field. (1) Air blower; (2) feeder; (3) cyclone; (4) bag filter; (5) high-speed digital camera; (6) LED light; (7) computer.

their short axis; it can be determined by the variation of the angle between the long axis of the particles and the vertical direction. Particle revolution (ω_θ) is defined as the motion of a particle around the center of a cyclonic flow field; it can be determined by the ratio of the linear velocity, u_θ, (i.e., the tangential velocity) to the radius of revolution, r_θ.

Fig. 4(a–c) shows the test results of the revolution, self-rotation, and flipping velocity of particles in a gas cyclonic flow field. It can be seen that the inlet gas flow rate (Q) plays an important role in each kind of velocity; the greater the gas flow rate, the greater the velocity of revolution, self-rotation, and flipping, with the particle's self-rotation being affected the most by the inlet gas flow rate. Therefore, the movement velocity of particles in a cyclonic flow field can be controlled by regulating the inlet gas flow rate. The average values of the revolution, self-rotation, and flipping angular velocity of particles under different inlet gas flow rates are shown in Fig. 4(d). The relation of the three kinds of velocity is $\omega_m > \omega_n > \omega_\theta$. With an increase in inlet flow rate, the increased rate of the self-rotation angular velocity is obviously larger than that of revolution and flipping. The ratio of the flipping velocity to the revolution velocity is basically stable, at 3.7. Since the self-rotation speed is significantly affected by the inlet flow rate, the

D (mm)	75
$a \times b$ (mm^2)	30 × 44
d_o (mm)	33
d_u (mm)	37.5
L_o (mm)	37.5
L_s (mm)	150
L_u (mm)	60
L (mm)	372
θ (°)	9

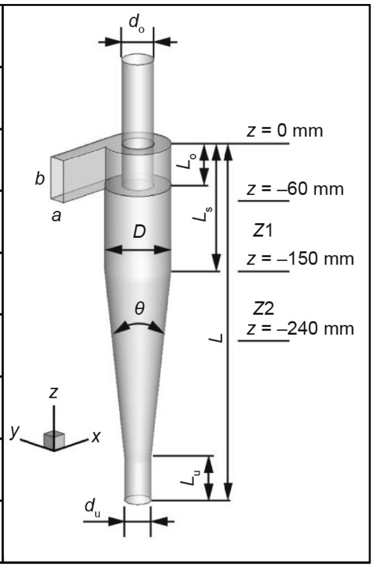


Fig. 2. Structural parameters of the tested cyclonic flow field.

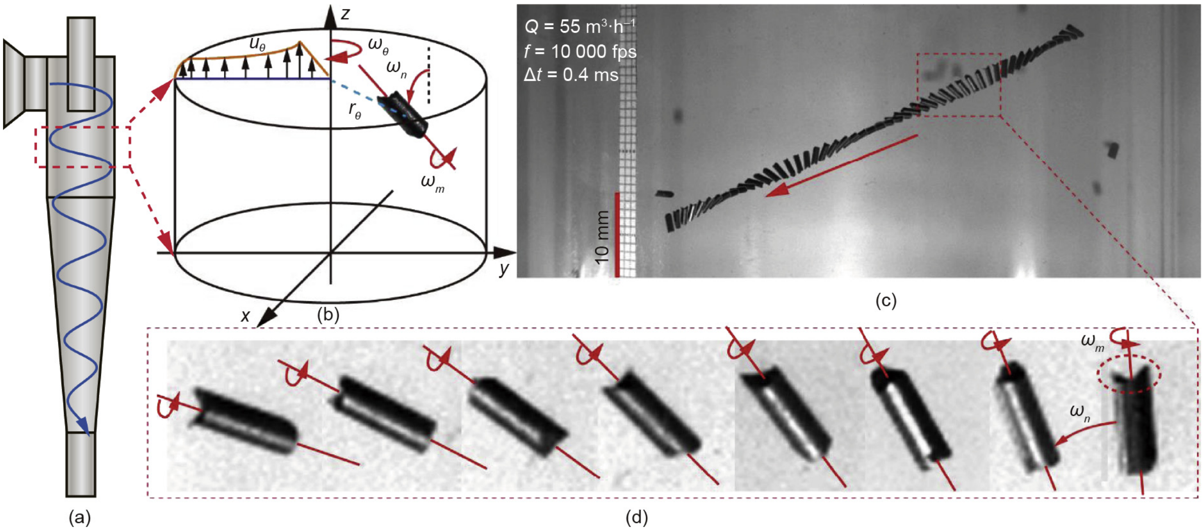


Fig. 3. Schematic diagram of (a) a cyclone and (b) the revolution, self-rotation, and flipping motion of particles in a cyclone; (c) the motion of the particles obtained by synthesizing high-speed photographs and (d) a detailed view. Q: inlet gas flow rate.

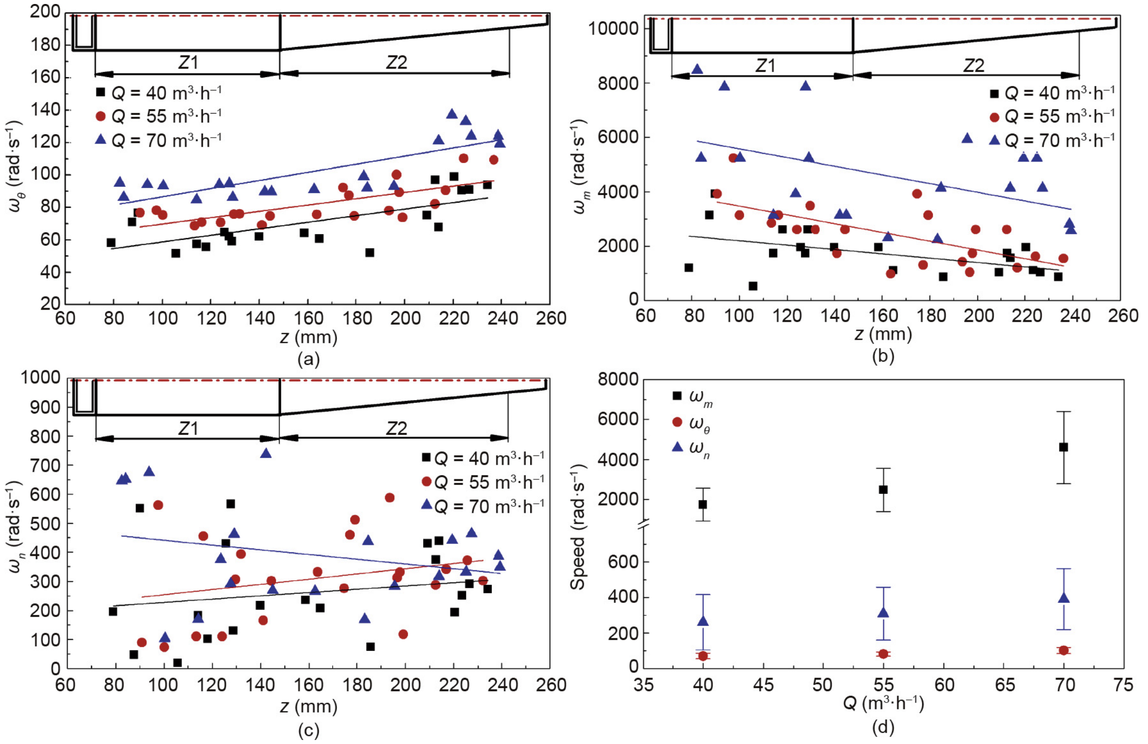


Fig. 4. Test results for the revolution, self-rotation, and flipping of particles in a gas cyclonic flow field. (a) Revolution; (b) self-rotation; (c) flipping; (d) comparison of three kinds of velocity.

ratio of the self-rotation velocity to the revolution velocity increases from 24.7 to 45.1.

The high-speed self-rotation (2000–6000 $\text{rad}\cdot\text{s}^{-1}$) and flipping (200–500 $\text{rad}\cdot\text{s}^{-1}$) of particles in a cyclonic flow field, as discovered by high-speed camera technology, provide favorable conditions for centrifugal removal and mechanical stripping of liquid pollutant from the pores of inorganic particles in organic waste liquid.

3. Organic waste liquid cyclonic gas stripping and the classification of inorganic particles through airflow acceleration

3.1. The concept behind the new technology

The new technique described in this paper relies on the development of cyclonic gas stripping and airflow acceleration classification inorder to achieve not only the efficient separation of organic wastewater and inorganic particles—thus strictly controlling the liquid content in the inorganic particles—but also the classification of particles according to porosity in order to permit the reuse of some of the particles with high porosity. The concept behind this technology is shown in Fig. 5. The preliminary separation of organic waste liquid and inorganic particles can be achieved through simple gravity settling or filtration separation; next, the particles containing organics are transported into the gas-stripping cyclone by high-temperature nitrogen gas. Because of their developed pore structure, inorganic particles inevitably carry large amounts of organic waste liquid in the pores, which is difficult to remove. A gas-stripping process of the liquid phase is carried out inside the cyclone, in which the centrifugal removal and mechanical stripping of the liquid phase from particle pores are enhanced by the high-speed self-rotation and flipping of particles. The rapid updating of a mass transfer interface can be achieved to accelerate the mass transfer rate, thus allowing the liquid phase in particles to be removed quickly and efficiently. The particles carried in the gas are separated by a cyclone and the gaseous organics are recovered by condensation; the purified gas can be circulated in the system.

After liquid removal, the particles have different degrees of porosity because of the different amounts of pollutants in the pores; thus, they have different reuse values. The direct result is that the particles have different particle densities. Research shows that particles with different densities have different acceleration characteristics in airflow [25–27]. The airflow acceleration classification method passes pulsating airflow with a positive cosine waveform into a vertical sorting column. This produces different accelerations due to the different response rate of particles with different densities to pulsating airflow, resulting in different displacements. Periodic amplification is performed under the action of pulsating fresh airflow. This magnifies the difference in the acceleration characteristics of particles with different densities in pulsating airflow, so that inorganic particles can be efficiently classified according to porosity.

3.2. Application in Sinopec's first ebullated-bed hydro-treatment demonstration unit for residual oil

In order to achieve the efficient use of heavy residual oil, the first ebullated-bed hydro-treatment demonstration unit for residual oil (i.e., the Sinopec Technology Residual Oil New Generation, or STRONG), with independent intellectual property rights, was jointly developed by the Sinopec Dalian (Fushun) Research Institute of Petroleum and Petrochemicals, the Sinopec Luoyang Petrochemical Engineering Corporation, the Sinopec Jinling Petrochemical Corporation, and the East China University of Science and Technology. The construction of a 50 000 $\text{t}\cdot\text{a}^{-1}$ industrial demonstration unit has been completed, along with the long-term operation of the experiment. Meanwhile, a corresponding experiment involving the cyclonic gas stripping of organic waste liquid and the recovery of high-activity catalysts by means of airflow acceleration classification has been completed.

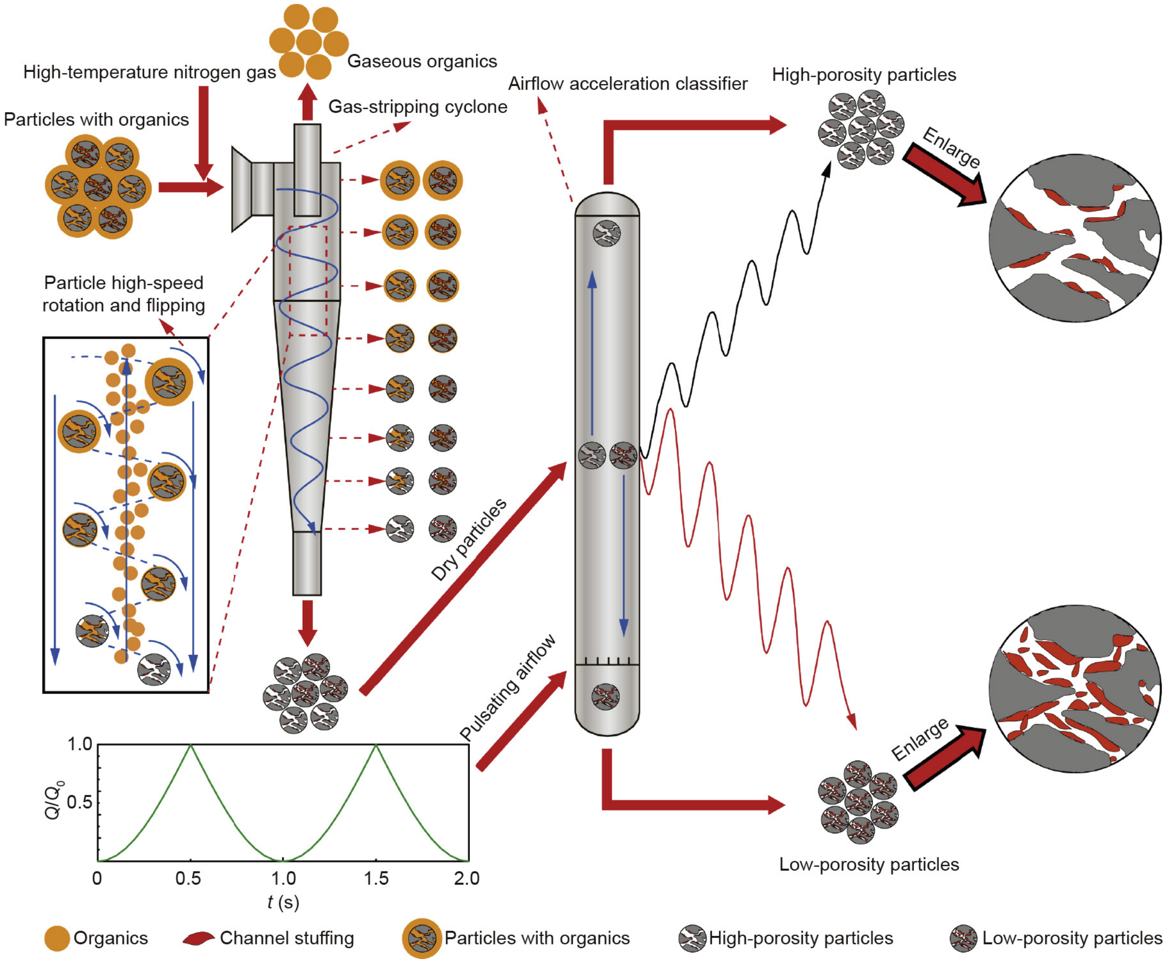
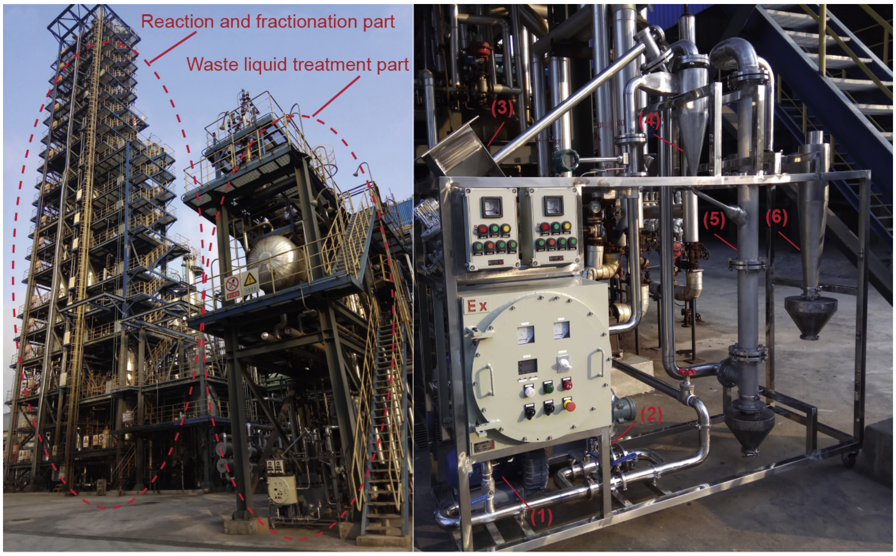


Fig. 5. Schematic diagram of organic waste liquid cyclonic gas stripping and airflow acceleration classification techniques for inorganic particles. Q_0: initial gas flow rate.

Fig. 6 provides a photograph of the industrial demonstration unit for the ebullated-bed hydro-treatment processing of 50 000 t of residual oil per year, along with a photograph of the accompanying device for the cyclonic gas stripping of organic waste liquid and the recovery of high-activity catalysts by means of airflow acceleration classification. The main components of the



(a) (b)

Fig. 6. (a) The industrial demonstration unit for the ebullated-bed hydro-treatment of residual oil. (b) The installation used for cyclonic gas stripping and airflow acceleration classification of high-activity catalysts: (1) blower; (2) pulsating airflow generator; (3) screw feeder; (4) gas-stripping cyclone; (5) airflow acceleration classifier; (6) cyclone separator.

discharged organic waste liquid are diesel and residual oil. The organic waste liquid, which contains 40 wt% of the porous catalyst particles, undergoes preliminary separation between the oil phase and the catalyst particles using simple gravity sedimentation. However, the catalyst particles still carry 31.8 wt% of the oil phase after gravity sedimentation; therefore, the direct discharge of these spent catalysts not only pollutes the environment, but also wastes oil resources. Due to the online addition of catalysts, the catalysts in the ebullated bed are in a state of full back mixing, which results in a large number of newly added, high-activity catalysts being directly discharged along with the spent catalysts. This not only causes an increase in effluent hazardous waste and a high processing cost, but also leads to a great waste of catalyst resources. In addition, in order to maintain the balanced activity of the catalyst in the reactor, it is necessary to continuously add the same amount of fresh catalyst as the effluent catalyst, which results in a large consumption of fresh catalysts. Thus, the highly efficient removal of oil and the recovery of high-activity catalysts from catalyst-containing organic waste liquid are the keys to the development of ebullated-bed technology.

Fig. 7 shows the oil-removal efficiency of cyclonic gas stripping under different temperatures. The initial oil content of the spent catalyst (with a mass flow rate of 24 kg·h^{-1}) after sediment separation and decantation is 31.8%. The oil content can be reduced to about 3% after cyclonic gas stripping when the gas temperature exceeds 300 °C. The minimum oil content can be reduced to 1.7%, and the corresponding oil-removal efficiency can reach 95.6%. Fig. 8 shows the state of the catalyst particles before and after cyclonic gas stripping; it can be seen that the catalyst particles change from a state of agglomeration with liquid oil to dry powders after cyclonic gas stripping. Most of the oil carried in catalyst particles has been separated, and the particles have great monodispersity and mobility.

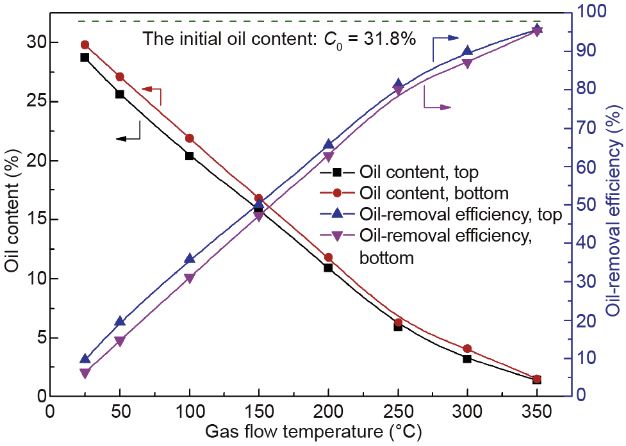


Fig. 7. Oil-removal efficiency of cyclonic gas stripping under different temperatures.

Furthermore, we carried out an airflow acceleration classification experiment on the catalysts discharged from the industrial demonstration reactor after the oil was removed, and were able to obtain 30% of the high-activity catalyst. As the waste came from an industrial demonstration unit, the catalysts had only been added six times and discharged five times; the residence times for all the discharged catalysts in the reactor were relatively short, and most of the catalysts had a low degree of deactivation, resulting in only a small difference in the activity of all discharged catalysts. We analyzed the physical properties of the catalyst particles before and after airflow acceleration classification. The results are shown in Table 1. The average particle density of the original spent catalysts was 1.813 g·mL^{-1}, and the average particle density of the high-activity catalysts selected by airflow acceleration classification was lower, at 1.705 g·mL^{-1}. The specific surface area and pore volume of the selected high-activity catalysts were, respectively, 2.17 and 2.75 times greater than those of the original spent catalysts. In addition, the carbon (C) and hydrogen (H) content was significantly decreased, whereas the active metal content was increased. The porosity and specific surface area of the sorted high-activity catalysts appeared to be improved, so that these catalysts would theoretically have a higher activity. These results verified the feasibility of applying airflow acceleration classification to the sorting of high-activity catalysts discharged from an ebullated bed.

We also evaluated the activity of the original spent catalysts and that of the selected high-activity catalysts in a micro reactor. The sulfur (S) content in the raw oil was 6.08%, the residual carbon content was 23.34%, the metal nickel (Ni) and vanadium (V) content was 168.5 μg·g^{-1}, and the yield of residual oil over 500 °C was 94.4%. The reaction temperature was 425 °C and the pressure was 14.5 MPa; the reaction time was 1 h, and the volume ratio of oil to catalysts was 13:1. We analyzed the oil after the reaction in order to obtain the activity of the catalysts; the results are shown in Table 2. It can be seen that the spent catalysts were

Table 1
Physical properties of catalysts before and after airflow acceleration classification.

Physical property	Original spent catalysts	High-activity catalysts
Oil content (%)	31.8	1.7
Particle density (g·mL^{-1})	1.813	1.705
Specific surface area (m^2·g^{-1})	32.1	69.5
Pore volume (cm^3·g^{-1})	0.16	0.44
Carbon content (%)	22.87	11.69
Hydrogen content (%)	3.04	1.35
Molybdenum content (%)	0.71	0.97
Nickel content (%)	2.4	3.4
Vanadium content (%)	10	14

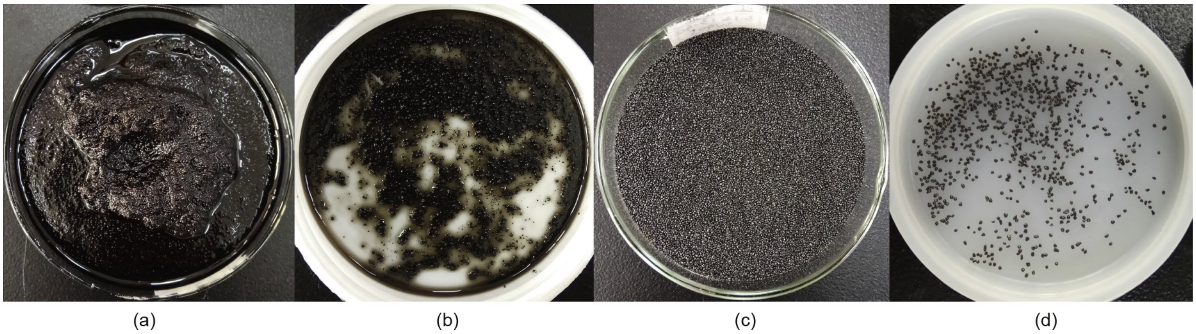

(a) (b) (c) (d)

Fig. 8. State of (a) catalysts and (b) particles before treatment; state of (c) catalysts and (d) particles after cyclonic gas stripping.

Table 2
Catalyst activity for different catalysts.

Performance	High-activity catalysts	Low-activity catalysts	Original spent catalysts	Fresh catalysts
HDS	55.4%	50.2%	51.6%	81.4%
HDCCR	62.5%	63.0%	61.9%	66.3%
HDM (Ni + V)	96.7%	97.0%	96.8%	98.0%
Yield of residual over 500 °C	65.6%	64.8%	64.2%	58.3%

HDS: hydrodesulfurization; HDCCR: hydro-Conradson carbon residue; HDM: hydrodemetallization.

sorted based on differences in particle density; the hydrodesulfurization (HDS) activity of the selected high-activity catalyst particles was obviously improved. Due to the short operating time of the reactor and the insufficient residence time of the spent catalysts, the hydro-Conradson carbon residue (HDCCR) activity and the hydrodemetallization (HDM, i.e., of Ni and V) activity had not yet become inactivated; therefore, there was only a small difference between the selected high-activity catalysts and the original spent catalysts. With an extension of the operating time, the difference in catalyst density would increase, and the effect of airflow acceleration classification would become more obvious.

3.3. Comparisons between cyclonic gas stripping and fixed-bed stripping

The Shenhua Group Co., Ltd., introduced the Axens Group's patented T-STAR ebullated-bed hydrogenation technology to a hydrogenation stabilization device, thus adding fixed-bed stripping technology to the treatment of organic waste with high concentrations of catalyst particles. The T-STAR technology is used to intermittently strip out oily spent catalysts, with a single gas-stripping batch time of more than 2 h. After de-oiling, the catalysts are all discharged without reusing or sorting, even though there are a large number of spent catalysts with high activity. Fig. 9 and Table 3 show a comparison of oily catalyst treatment by the T-STAR and STRONG technologies. The STRONG technology changes the fixed-bed gas stripper to a gas-stripping cyclone, which results in continuous processing rather than intermittent operation. The high-speed self-rotation and flipping of particles in the cyclonic flow field greatly improved the centrifugal removal and mechanical stripping of the organic solution (oil) in the catalyst pores, thus improving the oil-removal efficiency, shortening the stripping time, and reducing energy consumption. Furthermore, the new technology realizes the classification and reuse of

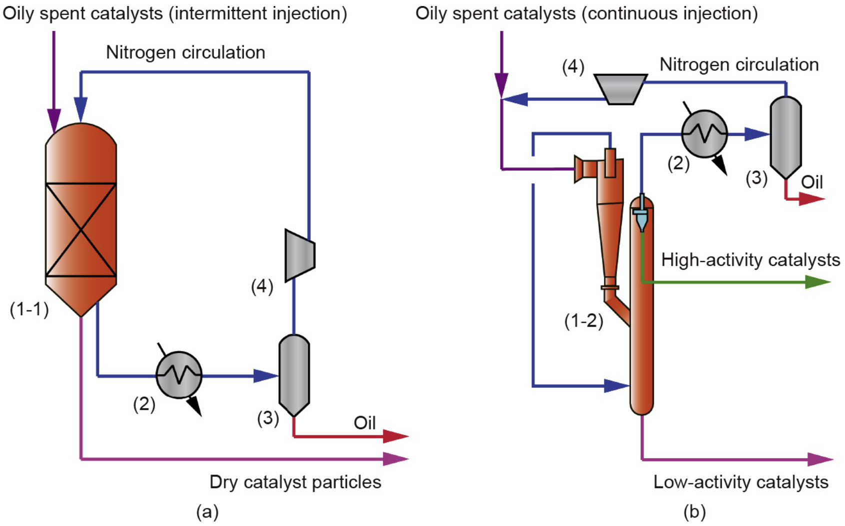
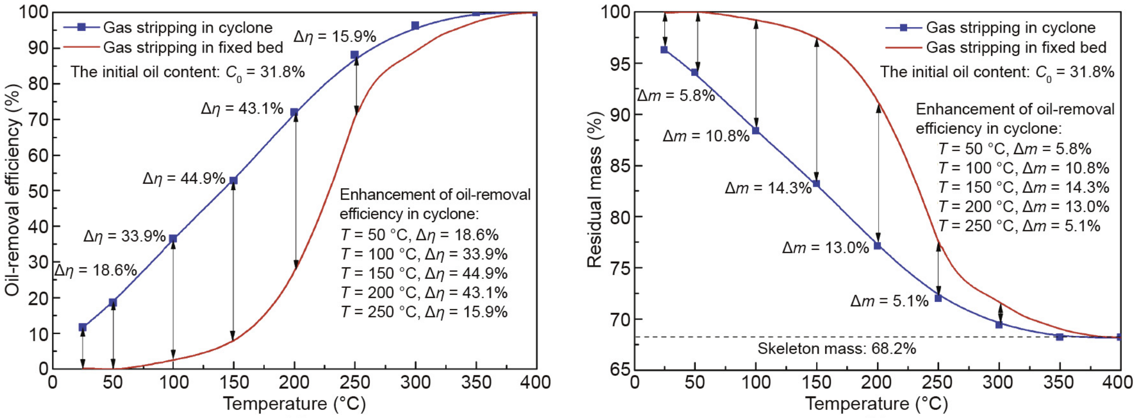


Fig. 9. A process comparison of oily spent catalyst treatment by (a) T-STAR and (b) STRONG. (1-1) Gas-stripping fixed bed; (1-2) gas-stripping cyclone and airflow acceleration classifier; (2) heat exchanger; (3) oil-gas separator; (4) compressor.

Table 3
A technical comparison of oily catalyst treatment by T-STAR and STRONG.

Performance	T-STAR (Axens, USA)	STRONG (Sinopec, China)
Operation method	Intermittent	Continuous
Oil removal	Fixed-bed gas stripping	Cyclonic gas stripping; the high-speed self-rotation and flipping of the particles in the cyclonic flow field can greatly improve the centrifugal removal and mechanical stripping of pore oil
Catalyst classification	None; all the catalyst particles are discharged	Can achieve the classification and reuse of high-activity catalyst particles; reduces the fresh catalyst consumption of the device
Oil-removal efficiency	8.2% (150 °C) 28.4% (200 °C) 71.5% (250 °C) 89.4% (300 °C)	53.1% (150 °C) 72.1% (200 °C) 87.6% (250 °C) 96.1% (300 °C)
Stripping time	7200 s	10 s
Energy consumption	Processing time is long, high energy consumption	The high-speed self-rotation and flipping of catalysts enhanced the cyclonic gas stripping, leading to lower energy consumption



(a) (b)

Fig. 10. A comparison of cyclonic gas stripping and fixed-bed gas stripping. (a) Oil-removal efficiency; (b) residual mass of spent catalysts. η: oil-removal efficiency; m: residual mass.

catalysts with high activity, and thereby reduces fresh catalyst consumption and solid waste emission.

Fig. 10 shows a comparison of oily catalyst treatment by means of cyclonic gas stripping and fixed-bed gas stripping under different temperatures. It can be seen that at the same temperature, the oil-removal efficiency of cyclonic gas stripping is higher than that of fixed-bed gas stripping. In particular, at 150 °C, the oil-removal efficiency of the fixed bed is less than 10%, whereas the efficiency of the cyclone is more than 50%—higher than that of the fixed bed by 44.9%; correspondingly, the residual mass of the particles of cyclonic gas stripping is lower than that of the fixed bed by 14.3%. The removal efficiency of the cyclone at the same temperature is higher than that of the fixed bed, indicating that the mechanical action, including the high-speed self-rotation and flipping of the particles in the cyclonic flow field, greatly improved the centrifugal removal and mechanical stripping of oil adhering to the catalysts, and particularly of the oil in the particles' micro pores.

Fig. 11 shows the oil-removal efficiency of cyclonic gas stripping and fixed-bed gas stripping over different stripping times. It can be seen that 80% oil-removal efficiency can be realized in 6.5 s with cyclonic gas stripping, but the same efficiency requires 1592.2 s with fixed-bed gas stripping. Similarly, 95% oil-removal efficiency can be realized in 8.4 s of cyclonic gas stripping, whereas fixed-bed gas stripping takes 1956.5 s. These results show that cyclonic gas stripping not only enhances the oil removal of oily spent catalyst, but also greatly shortens the gas-stripping time and reduces the energy consumption.

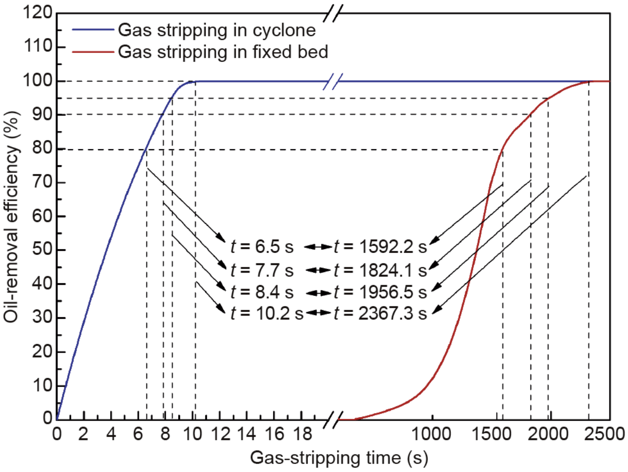


Fig. 11. A comparison of the gas-stripping time of cyclonic gas stripping and that of fixed-bed gas stripping.

4. Industrial amplification of the new technology in a 2×10^6 $t{\cdot}a^{-1}$ ebullated-bed hydro-treatment process for residual oil

Based on an industrial demonstration unit experiment for 50000 $t{\cdot}a^{-1}$ of ebullated-bed hydro-treated residual oil, a technical proposal was put forward regarding the use of this process to control discharged organic waste liquid and recover inorganic particles in 2×10^6 $t{\cdot}a^{-1}$ of ebullated-bed hydro-treated residual oil. The process flow is shown in Fig. 12. The installation discharged 15 $t{\cdot}d^{-1}$ of organic waste liquid containing a high concentration of catalysts—specifically, it contained 8856 kg of oil and 6144 kg of catalyst particles. The implementation of this proposal was an effective way to treat organic waste containing a high concentration of catalyst particles that was discharged from an ebullated bed. The cyclonic gas-stripping technology can realize highly efficient separation of the organic waste liquid from the inorganic particles, and strictly controls the liquid content of the inorganic particles, and especially the liquid in the pores. Airflow acceleration classification permits the highly efficient classification of catalyst particles according to activity, and allows high-activity catalysts to be separated out for reuse; in this way, it reduces the consumption of fresh catalysts and the solid waste emissions of the plant in question.

Table 4 shows the products of the organic waste liquid treatment of the ebullated-bed hydro-treatment for residual oil with a processing capacity of 2×10^6 $t{\cdot}a^{-1}$. The implementation of this new technology is estimated to recover 3100 $t{\cdot}a^{-1}$ of diesel fuel and 647 $t{\cdot}a^{-1}$ of high-activity catalyst. It will also reduce the consumption of fresh catalyst by 518 $t{\cdot}a^{-1}$. Considering that the price of diesel oil is 3000 CNY$\cdot t^{-1}$ and that of fresh catalyst is 60000 CNY$\cdot t^{-1}$, and deducting a running material and power consumption of 3.1 million CNY per year, the direct economic benefits of this technology can be as high as 37.28 million CNY per year. In addition, it can reduce the solid hazardous waste emissions of the plant by 30%. This new technology thus provides remarkable economic, social, and environmental benefits.

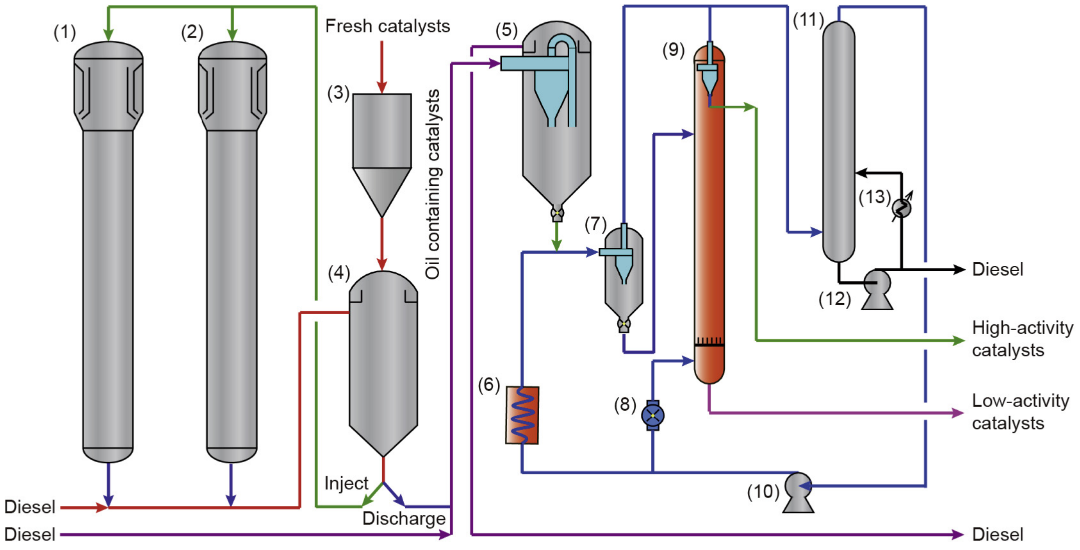


Fig. 12. The process flow for the separation and recovery of discharged organic waste from ebullated-bed hydro-treatment for residual oil with a processing capacity of 2×10^6 t·a^{-1}. (1,2) Ebullated-bed reactor; (3) metering tank; (4) adding tank; (5) activating hydrocyclone; (6) heater; (7) gas-stripping cyclone; (8) pulsating airflow generator; (9) airflow acceleration classifier; (10) blower; (11) nitrogen scrubber tower; (12) cooling pump; (13) condenser.

Table 4
The products of the organic waste liquid treatment of ebullated-bed hydro-treatment for residual oil with a processing capacity of 2×10^6 t·a^{-1}.

Product	Main indicators	Production (kg·h^{-1})	Production (t·a^{-1})	Usage
Recycled oil	Diesel oil containing asphaltene and resin	369	3100	Device recycling
High-activity catalysts	Accounts for 30% of the spent catalyst; the average activity is higher than 80% of fresh catalyst activity	77	647	Device reuse
Low-activity catalysts	Accounts for 70% of the spent catalyst; the oil content is less than 2%	181	1520	Metal recycling

5. Conclusions

Based on cyclonic gas stripping and airflow acceleration classification, this study developed a novel separation-and-recovery technology for organic waste liquid with a high concentration of inorganic particles. This technology was successfully applied to Sinopec's first ebullated-bed hydro-treatment unit for residual oil. The main conclusions can be summarized as follows:

(1) The high-speed self-rotation and flipping of particles in a three-dimensional cyclonic turbulent field was examined using a synchronous high-speed camera technique. The self-rotation speed was found to reach 2000–6000 rad·s^{-1}, which is 24.7–45.1 times greater than the revolution speed.

(2) A cyclonic gas-stripping method was invented to remove organic matter from the pores of particles, based on particle self-rotation. Compared with the T-STAR fixed-bed gas-stripping technology designed in the United States, the maximum liquid-removal efficiency of catalyst particles by STRONG is 44.9% greater at the same temperature.

(3) An airflow acceleration classification method was performed to achieve the classification and reuse of particles according to their porosity. The results of the operation of the industrial demonstration show that the selected high-activity catalysts can be reused.

(4) A technical proposal was put forward regarding the use of this new method for the control of organic waste liquid and the classification recovery of inorganic particles in 2×10^6 t·a^{-1} of oil produced by the ebullated-bed residual oil hydro-treating process. It is estimated that this process can recover 3100 t·a^{-1} of diesel fuel and 647 t·a^{-1} of high-activity catalyst.

The results indicate that this method provides remarkable economic, social, and environmental benefits, and has broad application prospects in the petrochemical industry.

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Compliance with ethics guidelines

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Nomenclature

D	Diameter of cyclone swirl chamber (mm)
d_o	Diameter of cyclone vortex finder (mm)
d_u	Diameter of underflow orifice (mm)
a	Cyclone inlet width (mm)
b	Cyclone inlet height (mm)
L_o	Length of cyclone vortex finder (mm)
L_s	Length of cyclone swirl chamber (mm)
L_u	Length of cyclone underflow pipe (mm)
L	Total length of cyclone (mm)
ω_0	Speed of particle revolution in cyclone (rad·s^{-1})
ω_m	Speed of particle self-rotation in cyclone (rad·s^{-1})
ω_n	Speed of particle flipping in cyclone (rad·s^{-1})

References

[1] Hu G, Li J, Zeng G. Recent development in the treatment of oily sludge from petroleum industry: a review. J Hazard Mater 2013;261(13):470–90.

[2] Xu N, Wang W, Han P, Lu X. Effects of ultrasound on oily sludge deoiling. J Hazard Mater 2009;171(1–3):914–7.

[3] Mrayyan B, Battikhi MN. Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge. J Hazard Mater 2005;120(1–3):127–34.

[4] Schwab AP, Su J, Wetzel S, Pekarek S, Banks MK. Extraction of petroleum hydrocarbons from soil by mechanical shaking. Environ Sci Technol 1999;33(11):1940–5.

[5] Armor JN. A history of industrial catalysis. Catal Today 2011;163(1):3–9.

[6] Silvy RP. Future trends in the refining catalyst market. Appl Catal A Gen 2004;261(2):247–52.

[7] Furimsky E. Spent refinery catalysts: environment, safety and utilization. Catal Today 1996;30(4):223–86.

[8] Weber S, Leuschner P, Kämpfer P, Dott W, Hollender J. Degradation of estradiol and ethinyl estradiol by activated sludge and by a defined mixed culture. Appl Microbiol Biotechnol 2005;67(1):106–12.

[9] Liu Y, Wang HL, Xu YX, Fang YY, Chen XR. Sludge disintegration using a hydrocyclone to improve biological nutrient removal and reduce excess sludge. Separ Purif Tech 2017;177:192–9.

[10] Yang Q, Li ZM, Lv WJ, Wang HL. On the laboratory and field studies of removing fine particles suspended in wastewater using mini-hydrocyclone. Separ Purif Tech 2013;110(23):93–100.

[11] Zhao K, Bai J, Zeng Q, Zhang Y, Li J, Li L, et al. Efficient wastewater treatment and simultaneously electricity production using a photocatalytic fuel cell based on the radical chain reactions initiated by dual photoelectrodes. J Hazard Mater 2017;337:47–54.

[12] Neyestani M, Dickenson E, McLain J, Robleto E, Rock C, Gerrity D. Impacts of solids retention time on trace organic compound attenuation and bacterial resistance to trimethoprim and sulfamethoxazole. Chemosphere 2017;182:149–58.

[13] Li JP, Yang XJ, Ma L, Yang Q, Zhang YH, Bai ZS, et al. The enhancement on the waste management of spent hydrotreating catalysts for residue oil by a hydrothermal-hydrocyclone process. Catal Today 2016;271(4):163–71.

[14] Xue Y, Zhang Y, Zhang Y, Zheng S, Zhang Y, Jin W. Electrochemical detoxification and recovery of spent SCR catalyst by *in-situ* generated reactive oxygen species in alkaline media. Chem Eng J 2017;325:544–53.

[15] Toulhoat H, Szymanski R, Plumail JC. Interrelations between initial pore structure, morphology and distribution of accumulated deposits, and lifetimes of hydrodemetallisation catalysts. Catal Today 1990;7(4):531–68.

[16] Rana MS, Sámano V, Ancheyta J, Diaz JAI. A review of recent advances on process technologies for upgrading of heavy oils and residua. Fuel 2007;86(9):1216–31.

[17] Menoufy MF, Ahmed HS. Treatment and reuse of spent hydrotreating catalyst. Energ Source Part A 2008;30(13):1213–22.

[18] Merino J, Bucalá V. Effect of temperature on the release of hexadecane from soil by thermal treatment. J Hazard Mater 2007;143(1–2):455–61.

[19] Ayen RJ, Swanstrom CP. Low temperature thermal treatment for petroleum refinery waste sludges. Environ Prog Sustain 1992;11(2):127–33.

[20] Al-Salem SM, Antelava A, Constantinou A, Manos G, Dutta A. A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). J Environ Manage 2017;197:177–98.

[21] Singh R, Gbordzoe E. Modeling FCC spent catalyst regeneration with computational fluid dynamics. Powder Technol 2017;316:560–8.

[22] Leyva C, Ancheyta J, Mariey L, Travert L, Maugé F. Characterization study of NiMo/SiO_2-Al_2O_3 spent hydroprocessing catalysts for heavy oils. Catal Today 2014;220–222(5):89–96.

[23] Rana MS, Ancheyta J, Sahoo SK, Rayo P. Carbon and metal deposition during the hydroprocessing of Maya crude oil. Catal Today 2014;220–222(4):97–105.

[24] Angeles MJ, Leyva C, Ancheyta J, Ramírez S. A review of experimental procedures for heavy oil hydrocracking with dispersed catalyst. Catal Today 2014;220–222(9):274–94.

[25] Jackson CR, Stessel RI, Peirce JJ. Passive pulsing air-classifier theory. J Environ Eng 1988;114(1):106–9.

[26] Everett J, Peirce JJ. Effect of feed rate and classifier height on air classification. J Environ Eng 1990;116(4):735–45.

[27] Duan C, Li H, He J, Zhao Y, Dong L, Lv K, et al. Experimental and numerical simulation of spent catalyst separation in an active pulsing air classifier. Sep Sci Technol 2015;50(5):633–45.

[28] Huang Y, Li JP, Zhang YH, Wang HL. High-speed particle self-rotation for coating oil removal by hydrocyclone. Separ Purif Tech 2017;177:263–71.

[29] Huang Y, Wang HL, Chen YQ, Zhang YH, Yang Q, Bai ZS, et al. Liquid-liquid extraction intensification by micro-droplet rotation in a hydrocyclone. Sci Rep 2017;7(1):2678.