



# The enhancement on the waste management of spent hydrotreating catalysts for residue oil by a hydrothermal–hydrocyclone process

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## ABSTRACT

Nowadays, the disposal of spent catalysts caused growing concerns on the environmental status, human health and industrial safety. The non-regenerable catalysts were either sent to metal reclaimers or disposed of in commercial landfills. The de-oiling and the following mechanical (hydraulic) separation are essential operations, which will minimize the amount of the spent catalysts as well as control the toxic substances deposited on the used catalysts. In the present study, a hydrothermal–hydrocyclone process was proposed to enhance the management of the waste catalyst for residue oil hydro-treating. Under the optimal conditions, the removal efficiencies of the contaminated hydrocarbons for the artificial and real system were 93.5% and 70.3%, respectively.

The enhancement of de-oil was originated from the self-rotation behavior of the catalyst particles. The rotation speed was estimated to be ~6870 rad/min by using the high-speed digital imaging and the numeric calculation. The application of hydrocyclone and the design process can also be used for the treatment of other solid wastes including contaminated soil, oily sludge and so forth. Moreover, it indicated that on the basis of the throughout understanding on the flow characteristics, the traditional operational equipment could be well manipulated in the treatment of environmental pollution.

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## 1. Introduction

The impact of catalysis and catalysts is substantial [1]. Today over 90% of all industrial processes are produced with the aid of catalysts including the refining of fossil fuel, the manufacture of chemicals, the production of synthetic materials and the treatment of the environmental pollutants. The consumption of the industrial catalysts was up to 800,000 ton/year in 2012, which brought the sales exceeding \$16.3 billion [2]. Among them, the refining catalyst accounts for about 24% of the world market and the catalysts for hydrotreating (HDT) and fluid catalytic cracking (FCC) contribute the largest share of refining catalysts [3]. The deactivation of the catalyst is inevitable and the spent catalysts generally discard as

the solid wastes. It is estimated that the total amount of spent HDT catalyst generated worldwide is 150,000–170,000 ton/year [4]. Potentially harmful constituents over a spent catalyst may be classified into two groups, (i) those that are present in the fresh catalyst, and (ii) those that are deposited during use [5]. Thus, from the aspect of environmental, health and safety, there is a demanding concern of the spent catalyst due to the catalyst itself or the deposited hazardous volatile or persistent organics [6].

Nowadays, the demand of heavy fuel oil as marine engineering fuel has decreased significantly, whereas, the need for light and clean fuel has moved toward the opposite direction. It has been reported that NiMo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixed oxide supported catalysts are suitable for such a purpose, because of their acidic and textural properties [7]. However, these catalysts would deactivate during time on stream mainly due to coke formation and poisoning [8]. About 20–30% of the initial surface area and pore volume was lost due to the coke deposition. Meanwhile, with the times on stream increases, more metal-sulfide compounds would deposit in the pores of the catalysts [9]. The deposition of coke, metal and oil

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would make the spent catalysts heavier than the fresh catalysts, which generates more industrial waste. For instance, the feedstock of the residue oil in 2015 will increase 6 times of that in 2010 [10,11]. More commercial units devoted to heavy oil hydroprocessing with moving beds, such as H-Oil and LC-Fining, which could compensate for catalyst deactivation through adding catalysts at the top of the reactor and withdrawing at the bottom [12]. The consumption of moving bed is larger than fixed bed. It is obvious that the quantity of the spent catalysts, especially that of HDT catalyst of residue oil, will greatly increase simultaneously.

The non-regenerable catalysts were either sent to metal reclaimers or disposed of in commercial landfills [13]. The de-oiling and the following mechanical (hydraulic) separation are essential operations for the management of spent HDT catalysts. The weight reduction of nearly 20% will be achieved and the toxic substances (such as PAHs, PCBs and PCPs) with high flexibility will be controlled [14]. Various techniques were proposed for the removal of oil and toxic organic compounds attaching on the surface of porous solid materials. These techniques were widely applied not only in the treatment of spent catalysts, but also in the management of other solid wastes, namely oily sludge, contaminated soil. Thermal treatment is one of the most popular techniques [15,16]. However, the overheating of the spent catalysts will lead to the sintering of the metal and take adverse effects on the reclamation of the metal. Specifically, the treatment temperature for the residue-oil contaminated system should be over 400 °C. The application of organic solvent extraction will facilitate the release of oil from the spent catalysts. But the recycle of the solvent is a necessary operation [17]. The hydrothermal method is a more versatile technique on the removal efficiency, the instrumental investment and the operational time. The addition of other reagents, such as NaOH and organic surfactants [18,19], will accelerate the release of oil and the application of ultrasonic or sparging air can also enhance the process significantly [20,21].

In the present research, the hydrothermal desorption was carried out in a novel two-step procedure, namely hydrothermal-hydroclone process. The spent catalysts were continuously treated by a stirring hydrothermal tank and a subsequent hydrocyclone. To the best of our knowledge, it is the first time a hydrocyclone was used for the management of spent catalysts. The artificial catalysts and the actual spent catalysts discarded from a pilot plant of residue-oil hydroprocessing in FRIPP (SINOPEC, China) were both applied as the model porous materials. Generally, hydrocyclones belong to a class of fluid–solid classifying devices that separate dispersed material from a fluid stream [22]. Compared with the traditional separation apparatus, such as filters and centrifuges, hydrocyclone is a powerful separation equipment with numerous advantages, such as large processing capacity, low cost, easy to scale up, and high stability of operation [23]. Additionally, it was concluded that the application of the hydrocyclone can greatly enhance the release of contaminated hydrocarbon from the contaminated catalysts due to the forced self-rotation of the catalyst particles within the hydrocyclone. The application of hydrocyclone and the design process can also be used for the treatment of other solid wastes, including contaminated soil, oily sludge and so forth.

## 2. Experimental

### 2.1. Materials

The commercial wash-oil from JLPEC (SINOPEC, China), 50 tabulated bed residue hydrocracking process (STRONG, Sinopec Technology of Residue Oil New Generation) was used for the simulation of the oil-containing catalysts. The physical chemical properties of the wash-oil were shown in Table 1. Two kinds of

**Table 1**  
Properties of the washing oil.

Parameter	Unit	Value
Density at 20 °C	kg/m <sup>3</sup>	1023.5
Density at 235 °C	kg/m <sup>3</sup>	727.31
Viscosity at 235 °C	cP	0.29498
Surface tension at 235 °C	dyne/cm	15.0951
Specific gravity (SPGR)	g/cm <sup>3</sup>	0.8743
Sulfide content	%	3.591
Nitrogen content	μg g <sup>-1</sup>	5500
Hydrogen content	%	10.2
Distillation range (ASTM D1160)	°C	588.2–1256.0

catalysts obtained from the pilot plant (4 L/day) in FRIPP (SINOPEC, China) were also applied in this study (see Table 2). FES-2 is the fresh catalyst used for the residue-oil hydrotreating and FEM-1 is the spent catalyst discarded from this pilot plant. DI water with the electrical resistivity of ~18.0 MΩ and chemicals of analytical reagent (AR) quality were used if without emphasis.

### 2.2. Experimental procedures and apparatus

The artificial spent catalyst was self-prepared of washing-oil and FES-2 by an immersing-leaching method due to the limited amount of the actual ones (FEM-1). With a liquid-to-solid ratio of 6:4, the mixture (FES-2 and washing oil) was continuously stirred under an agitation speed of 100 rad/min for 6 h at 95 °C. The washing oil was dumped and the contaminated catalysts were held in the dry air for 24 h at 40 °C before use. The obtained sample was sealed in dark at room temperature before use.

The sample was firstly washed by the boiling water in the hydrothermal tank then delivered into the hydrocyclone for the heterogeneous separation. In order to optimize the treatment conditions, the artificial spent catalyst of 100 g was loaded into the hydrothermal tank in batches. One assay of the solid–liquid mixture with the volume of 250–300 ml was pumped out into a glass breaker. After filtration with 0.22 μm Nafion<sup>®</sup> membranes, the solid samples were vacuum dried at 40 °C overnight. The oil content and the composition of the oil were analyzed then.

Under the optimal conditions, spent catalysts (both real and artificial) were continuously treated by the hydrothermal-hydrocyclone process using a self-designed experimental apparatus (seen in Scheme 1). It consisted of a hydrothermal tank (Φ 600 × 800 0.255 m<sup>3</sup>), a hydrocyclone (DN25 type, seen in Scheme 2) and a buffer tank (Φ 300 × 400, 0.030 m<sup>3</sup>). The spent catalyst was mixed with DI water and sent by the booster pump (Nikuni, 4025CTWF1-2SC) within the system. The setup of thermocouples (WSS411, Tianchuan Co. Ltd.), pressure meters (Y-100BF/MC, 0–0.6 MPa Shanghai Jiangyun Co. Ltd.) and the regulator valve (Gestra 5801, Gestra GmbH, Germany) can also be seen in Scheme 1. All the tubes used in this apparatus were made of stainless steel (316 L) with the diameter of 25 mm. The solid–liquid mixture was pump into the hydrothermal tank with the rate of 9 L/h. After 600 s, the control valve to the hydrocyclone was shifted on. The inlet rate

**Table 2**  
Properties of the spent catalysts.

Parameter	Unit	FEM-1	FES-2
Shape		Sphere	Sphere
Bulk diameter	mm	0.4–0.5	0.4–0.5
Stacking density	g ml <sup>-1</sup>	≥0.63	≥0.63
Matrix density	g ml <sup>-1</sup>	~3.0	~3.0
Wear index	%	≤2	≤2
Porous volume	ml g <sup>-1</sup>	≥0.65	≥0.65
Specific surface area	m <sup>2</sup> g <sup>-1</sup>	≥120	≥160
Chemical composite		Mo-Ni/γ-Al <sub>2</sub> O <sub>3</sub>	Mo-Ni/γ-Al <sub>2</sub> O <sub>3</sub>
Metal content	%	14.2	15.8

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