Regeneration method for spent FCC catalysts: Brief Review

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Abstract

Throughout refinement, catalysts are switched off in commercial catalytic processes. When they are not tuned, catalysts become dangerous. Deactivation catalyst is mostly wasted FCC catalyst as a result of heavy metal coke, poison, and sintering. Regenerating a deactivated catalyst could eliminate the metals while resurrecting the very desirable catalytic activity. While there are a few a variety of physical, chemical, and thermal treatment methods for removing metals, it is still difficult to discover reliable, effective, and cost-effective regeneration strategies for catalytic processes in commercial application. In addition, the effect of relevant reaction parameters on the route for regenerating utilized catalyst was investigated, and suggestions were made for the future of this research. This brief review offers an important evaluation of the material recently made publicly available on the reuse of used FCC catalyst by oxidation, gasification, and chemical processes, could potentially provide some insight into the development and improvement of catalysts as well as associated processes.

Keywords: Spent catalyst, regeneration, chemical, oxidation, gasification

1. Introduction

Around 80 percent of industrial operations today utilize the various applications and the various catalyst because of their advantages, include petrochemicals and fine chemicals, as well as air/wastewater treatment. But a significant downside is their inevitable deactivation, which occurs throughout a variety of time periods, from days to years [1]. As a result of the fast development and extensive use of catalysis technology, a number of catalysts are utilized in a variety of industrial processes. The catalysts are dumped as spent catalyst because they become poisoned or inactive after periods of operation. The quantity of various spent catalyst has increased by a factor of two every year. These spent catalyst typically contain important metals, and their characteristics depend on the catalysis procedures [2]. Due to its practicality, adaptability, and economic viability, FCC is the primary refinery process. It can transform high molecular, high boiling, and straight-chain alkane hydrocarbons into olefinic paraffinic gases and other products, including high-octane gasoline. On the active site of the catalyst, carbon exists as coke as a byproduct. FCC catalyst is in the form of a fine powder with a bulk density of 0.80 to 0.96 g/cm³ with an average particle size of 75 mm and an average surface area of 800 m²/g [3]. The presence of even a small quantity of metal deposits may stimulate the decomposition of coke, which can diminish yield and change the product's chemical makeup. This is true even when using FCC catalyst, which is great for cracking and producing various branched hydrocarbons. In order to get the desired results, various physical, chemical, and thermal methods were used [4, 8]. The contamination of FCC catalysts with Vanadium (V), Nickel (Ni), Iron (Fe), and Sodium (Na) has a negative impact and can affect the structure and performance of the catalysts, despite the fact that nitrogen and sulfur have fewer negative effects. Coking effect clogged pores results in major issues [8]. By choosing reaction conditions or by adding a gasifying agent, on the catalyst's surface, it is possible to minimize coke generation. Decrease the support's acidity to decrease coke deposition on oxide or sulfide catalysts and prolong catalyst life. Because this process is irreversible, It is essential to select the reaction conditions and catalyst quality to prevent heat degradation or sintering. By choosing a lower temperature, one may successfully avoid sintering, and by reducing water vapor, one can prevent crystallization and structural changes to the oxide support. The rate of sintering on the catalyst can also be slowed down by adding thermal stabilizers such higher melting noble metals [9].
Based on highly expensive active fresh catalysts and environmental concerns, this review offers a significant synopsis of the most recent advancements in the extensive research on various spent FCC catalyst management treatments. It studies the current tendency of the effectiveness treatment of spent FCC catalyst management and the influence of the regeneration of a spent FCC catalyst that has been deactivated.

2. An Overview of FCC spent catalyst Regeneration

Dufresne (2007) demonstrated that the annual global production of spent catalyst is between 150,000 and 170,000 tons [10]. Therefore, a 5 percent annual increase in catalyst use is anticipated to result in the production of 250,000 tons of wasted catalysts annually. Although there are several mechanisms behind this phenomena: Toxicity (Chemisorption of contaminants or by-products on active sites), fouling (carbonation or coke deposition), and/or degradation (chemical, physical or mechanical) Bartholomew, 2003. The regeneration techniques for spent FCC catalysts may be divided between two groups [13]. In the first group, following filtering, the catalyst is regenerated by washing and drying it at temperatures typically below 200 degrees Celsius. In the second, calcination alone or in conjunction with other processes is used [12]. Madhu et al. find that wasted catalysts must be calcined to reactivate the active site [13]. Boey et al. utilized the waste catalyst a minimum of three times with a purity of more than 96.5 percent. Before being reused, the spent catalyst was calcined at 900 °C for two hours and washed with methanol and n-hexane to remove the adsorbate [14].

2.1 Regeneration of the Oxidation

The most common approach for eliminating toxins is combustion treatment or burning, which often involves air, oxygen, or nitrous oxide-containing mixes [15]. Air-based oxidative treatments generally operate at temperatures between 400 and 600 °C, which may lead to irreversible chemical interaction of the catalyst with the water vapor produced [16]. This technique may produce OH and some other oxygenated radicals, hence enhancing mass transfer rates and chemical processes and enhancing the surface. The regeneration of spent FCC catalysts by hydrogen reduction was studied [17]. The procedure was also carried out at high temperatures (427 °C for many hours, followed by 482 °C for several hours), with identical outcomes to the oxidative process. According to studies Romain [1], Coked catalyst was regenerated using ozone to handle spent catalyst. The experiment was conducted in a reactor setup with a fixed bed. In the regeneration of spent catalyst utilizing temperature ozone-enriched air or oxygen at 150 °C, up to 74.3 percent coke was eliminated; however, temperatures over 150 °C temperature were not advantageous owing to the substantial restriction on ozone diffusion inside the catalyst. The speed of decoking was also enhanced by an increase in O3 concentration. The research investigated the regeneration of wasted catalysts with varying concentrations of O3 and the effects of increasing temperatures to eliminate coke.

Chen Jyh-Cheng'sl [2] study revealed that the conversion efficiencies of C3H8 by various regenerated Pt-Pd catalysts increased from 77 to 99 percent. The optimal regeneration conditions were discovered to be 52 pyro zone, 10 cm minutes, and 500 °C. The factors of regeneration, such as temperature, ozone concentration, and regeneration time, were examined. It was discovered that raising temperature may reduce the time required for contact operations, however higher temperatures are not beneficial and have limitations since they can affect catalyst sintering. Comparing the properties of deactivated and regenerated catalysts enables ozone regeneration to successfully eliminate the primary toxic species (carbon, metals, chloride, & sulfate) from spent catalysts.

Based on previous research, the oxidation treatment is preferred. Romaine and Chena show that regeneration using oxidation treatment, especially ozone, may significantly reduce toxicity and increase product conversion. Monitoring regeneration factors, such like temperature, which will result in a decrease in contact time processes, but should be accounted for, is vital. The emissions of hazardous gases such as ozone and ox nitride are strictly restricted.

2.2 The Regeneration of Gasification

Although coke oxidation is widely employed to recover inactive industrial catalysts, the coke cannot be appraised, and substantial amounts of CO2 are generated. Carbon dioxide is a greenhouse gas that leads to severe environmental concerns, including global warming. For instance, the regeneration of wasted catalysts with air combustion in FCC units generates between 40 and 45 percent of the CO2 produced by refineries [18].

The utilization of CO2 as a feedstock has attracted increased attention due to its positive impact also on global carbon balance. CO2 may operate as a moderate oxidizing agent in the Reverse Bouduard (RB) process, where it reacts with coke [19]. Figure 1 depicts the situation. Regeneration spent FCC catalysts, particularly those coked by CO2 gasification, may reduce CO2 to CO, there is beneficial for the carbon footprint. Carbon dioxide has been used to gasify coal, biomass, and sewage sludge [20]. Where Coffins a free active site and CO is the reacting carbon-oxygen surface complex, which is an occupied active site. According to this mechanism, the carbon-oxygen complex is originally produced either by dissociation of CO2 at a free active site, which results in the release of a CO/molecule. The carbon-oxygen combination then generates a newly accessible active site and an additional Carbon monoxide molecules [21]. These materials are beyond the scope of this study and are not studied further. CO2 gasification, which often occurs at temperatures exceeding 700 °C, is a strongly endothermic reaction that might destroy a framework of the catalyst or lead to sintering [22]. Consequently, the low reactivity of CO2 and the needed high reaction temperatures are the two fundamental restrictions for catalyst regeneration employing CO2 gasification. In contrary to steam gasification, CO2 gasification offers many advantages. CO2 is a gas, unlike steam, which must be evaporated prior to gasification. In
addition, at high temperatures, steam may destroy the Al-O binding of the catalyst, resulting in the failure of spent FCC catalyst [23]. Santos et al. [24] investigated the regeneration of spent FCC catalysts in a CO2 He system using temperature-controlled reactions from room temperature to one thousand degrees Celsius. They determined that the type of coke had a significant effect on the pace of gasification. With several substitutions, aliphatic and aromatic species were even more reactive with CO2. In addition, CO2 gasification may be correctly predicted at temperatures up from 600 to 940 °C with a first-order kinetic model. Even though O2 is many orders of magnitude more reactive than CO2, CO2 gasification mainly ever the less appear in the presence of O2. Based on the CO2 partial pressure, CO2 may also dominate the initial step of the catalysts regeneration, renewing the coked catalyst needed to improve heavy petroleum feeds. Wang et al. [25] studied the Carbon dioxide gasification reactivity between 8800 to 900 degrees Celsius. The findings indicated that increasing the temperature increased the zgasification rate, thus the rate declined significantly when coke conversion above 50 percent. This was in line with the findings of Santos et al. et al. [26]. The steam gasification rate for spent FCC catalyst being used vacuum residue cracking was shown to be relatively low, regenerated at temperatures below 700 degrees Celsius. Increasing the temperature to 800 degrees Celsius increased the rate of coke removal. The proportion of H2 and CO in the produced gas remained constant at 87 volume percent regardless of gasification temperature. The rate of steam gasification climbed initially, peaked at coke conversions between 5 and 20 percent, and then fell subsequently. It was investigated how O2 affects gasification activity and the composition of the resulting gas. During the coke removal from the FCC catalyst, the addition of 5% by volume of oxygen to the steam. When CO2 and H2 levels were significantly increased, gasification time was just marginally sped up. Gasification may be used to remove the coke that has accumulated on the catalyst, but it needs high temps and might harm the catalyst's structure. Hydrogen at high temperatures may also be utilized to remove toxins such as coke.

2.3 The Regeneration of Leaching
Diverse leaching regeneration processes often using hazardous chemicals such as chlorine, hydrogen sulfide, and strong acids have been employed to extract the metals Ni, V, and Fe from spent FCC catalyst. Describe the best effective method for eliminating contaminating metals from carbochlorination-used Spent FCC catalyst. Nonetheless, owing to excessive chlorination, catalytic activity was not recovered [27]. Heavy crude oils include nickel-containing compounds in their native state. Leaching acids are used to enhance the procedure for reactivating spent catalyst. Leaching is the process of extracting substances from solids by dissolving them in liquid. Acidic leaching is an extraction technique where acidic substances are used to grind and de-coke wasted FCC catalyst in order to recover metal. This table demonstrates how wasted FCC catalyst was regenerated with different chemical leaching and metal removal effects.

Table 1: Application varying acids treatment on effect of metals

<table>
<thead>
<tr>
<th>Type Acid</th>
<th>Recover metals</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combined acid that are (Acetic acid 998 percent, oxalic acid 99.6 percent, hydrochloric acid 36 percent)</td>
<td>Ni 37%</td>
<td>Production of the Light oil</td>
<td>Lu et al. [26]</td>
</tr>
<tr>
<td>Sulfuric Acid 96.1%, citric acid 99%</td>
<td>Ni 62%</td>
<td>Palm oil cracking to Biofuels</td>
<td>Istadi et al. [29]</td>
</tr>
<tr>
<td>Oxalic acid and sulfuric acid</td>
<td>Fe 36.2%</td>
<td>Enhanced spent RFCC catalyst under Ultrasound</td>
<td>Tian et al. [30]</td>
</tr>
<tr>
<td>Oxalic-acid/hydrogen-peroxide</td>
<td>V 91.36%</td>
<td>Enhanced spent RFCC catalyst under microwave-assisted conditions</td>
<td>Zheng et al. [31]</td>
</tr>
</tbody>
</table>

In this work, Lu et al. [28] reactivated fluid catalytic cracking (FCC) using a combine acid containing 98 percent acetic acid, 99.6 percent oxalic acid, and 36 percent hydrochloric. During a reactivation of Spentp FCC catalysts, the best conditions were particle size 40-100 m, 1.0 FWT) % HClL) S/L [=] 1/5 v,” leaching period 1.5 h at a temperature between: 25-50 °c, and attention to the volatile (oxalic/acetic acid at 50°C. Most heavy metals might be extracted under these circumstances. Ni is extracted at a rate of 37%, whereas molecular sieves retain the majority of their active components. With rising acidity, FCC catalyst particle size decreases [32-33]. The spent FCC catalyst treatment using 1% combined acid was smoother than the spent catalyst, and the framework of the spent catalyst was not compromised. Compared to spent catalysts, the catalytic performance of reactivated catalysts is significantly enhanced, and the light oil production is greater than that of new catalysts. Istadi, et al. [29] In an additional investigation, the reaction & modifying of the spent RFCC catalyst with sulfuric acid (96.1%) and citric acid (99%) as acids treatment was tested by altering the acid solution concentrations at 80 °C under stirring for three hours with a solid Xbox liquid ratio of (1:10) w/v [34]. This research indicates that sulfuric acid treatment is better to citric acid treatment for the removal of heavy metals from acid-affected catalysts. Using sulfuric acid, S(0.3)-RFCC and S(0.5)-RFCC samples removed up to 62% and 32% of Ni, respectively, but citric acid had no effect at the same concentration. It is believed that the differing acid strengths of the two acids explain this disparity. Citric acid is a mild organic acid opposed to sulfuric acid that is a strong inorganic acid. Strong acid immediately dissolves the catalyst’s metal contamination. Astuti et al. found in a prior research that sulfuric acid dissolves metals at a faster pace than citric acid [10]. The ratio of Bronstedtoq Lewis (B/L) is affected by sulfuric acid, whereas citric acid has the reverse effect. In addition, different acid types resulted in variations in the main chemical composition of the end product, with citric acid-
based FCC catalysts yielding more hydrocarbons than sulfuric acid-based catalysts. There is also a parameter of regeneration chemical known as the regeneration method is the processing leaching. Morris et al. [36] Mo, V, and Ni were extracted from used HPC catalysts utilizing H2SO4 and citric acid and ultrasonic agitation procedures in this work. Ultrasonic vibration improved the extraction of metal. Over ninety-five percent of all valuable metals were extracted at a short amount of time at a relatively low temps, made this cutting-edge technique essential for further research on metal extraction. Mitchel et al. [37] showed that adding ultrasound into acid leaching for the recovery of metals from a spent nickel hydrogenation catalyst supported by silica may result in favorable outcomes. After ultrasonic leaching for 2 hours at 60 degrees Celsius, Marafi et al. discovered the leaching rate of V was as high as 94.8 percent, which was 11.1% greater than that of traditional stirring leaching [38]. Oza et al. [39] discovered that utilizing ultrasonic technology, nickel could be recovered from used catalysts substantially quicker than through chelation. The efficient regeneration of spent FCCP catalyst is crucial for the commercialization and future development of the catalyst in order to extend its lifetimes. In addition, the optimal treatment of spent FCC catalyst would aid several industries in conserving energy required to renew the catalyst, hence reducing economic and environmental impacts.

3. Conclusion
The waste handling of spent FCC catalyst is essential for commercialization and future studies into increasing the catalyst's lifespan. In addition, the optimal management of spent FCC catalyst may aid many industrial refineries in saving energy throughout catalyst regeneration, thus mitigating any negative impacts on the environment and economic wealth. Chemical regeneration is one of the greatest applications for treating used catalysts, since it is more successful than other treatments at removing metal and is also more economically viable, as it is simple to manage on a laboratory and plant scale. Therefore, it may be feasible to integrate treatments with each treatment also with specific metal removal, but further study is required. In recent years, numerous treatment strategies for spent FCC catalysts have been proposed, and promising results have been obtained. It is essential to recognize that further technical obstacles must be overcome in order to develop a viable technique for large-scale applications in the refineries sector. There are three techniques that commercial to handle the spent catalyst. Regeneration and rejuvenation, for instance, are utilized to remove and restore valuable metals from of the catalyst surface. Among them is the oxidation, gasification, and chemical regeneration dissolution. Chemical regeneration is performed by acidic treatment, which utilizes mainly lower temperatures because to the restricted volatility of the acids, hence using less energy than oxidation and gasification regeneration. In an effort to reduce air pollution and soil contamination, utilized FCC catalysts may convert plastics waste into chemical feedstock or fuels. Landfilling would be the last option if these methods were unsuccessful. Whereas only non-hazardous spent catalyst may be discarded, they must be treated to remove these harmful substances.

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