



Review

Oil refining spent catalysts: A review of possible recycling technologies



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ABSTRACT

The aim of this review paper is to analyse the current management of spent fluid catalytic cracking catalysts (FCCCs) and the relevant possible reuse and recycling methods in order to avoid landfilling. FCCCs are used in refining processes for conversion of vacuum gas oil into more valuable gasoline blend components and other products. Every year the worldwide supply is estimated at about 840,000 t (Letzsch, 2014). The main recycling technique found in literature for spent FCCCs entails their use as raw material for concrete and mortar production as partial replacement of sand and cement powder. Other minor applications include their use as catalysts for plastic and biomass pyrolysis and gasification or for production of synthetic fuels. Despite their importance, these processes have not been widely developed at industrial scale. Disposal to landfill or use for concrete blend is still the main choice for the handling of spent catalysts, despite the content of rare earths elements and sometimes other interesting metals like vanadium and nickel that could be recovered. Nevertheless, in the future these catalysts will represent an interesting source for secondary raw materials, considering the scarcity of rare earth elements and shortage of supply, due to the fact that production is concentrated only in few countries. In this perspective, the recovery of rare earth elements will be of great interest to countries that do not own primary ores. Future research work is expected to lead to economical processes that reach a complete recycling in order to avoid landfilling. This action could be helped by the adoption of new environmental regulations which will heavily charge landfilling as final disposal.

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Nomenclature

BET	Brunauer Emmett Teller
BTX	benzene toluene xylene
CFP	catalytic fast pyrolysis
CYANEX 272	bis(2,4,4-trimethylpentyl) phosphinic acid
D2EHPA	di-(2-ethylhexyl) phosphoric acid
DTA	differential thermal analysis
EPA	environmental protection agency
EWC	European waste catalogue
FCC	fluid catalytic cracking
FCCC	fluid catalytic cracking catalyst
FOB	free on board
FTS	Fischer–Tropsch synthesis
GC–FID	gas chromatography–flame ionisation detector
GC–MS	gas chromatography–mass spectrometry
GC–TCD	gas chromatography–thermal conductivity detector
GTL	gas-to-liquid
HDC	hydrocracking
HDPE	high-density polyethylene
HDS	hydrodesulphurisation
HVGO	heavy vacuum gas oils
IFB	interconnected fluidised bed
LDPE	low-density polyethylene
LPG	liquefied petroleum gas
PE	polyethylene
PP	polypropylene
PS	polystyrene
PVC	polyvinyl chloride
REE	rare earth element
REO	rare earth oxide
SEM	scanning electron microscopy
TCLP	toxicity characteristic leaching procedure
TGA	thermo-gravimetric analysis
TPR	temperature programmed reduction
UV–vis	ultraviolet–visible
VGO	vacuum gas oil
WGS	water–gas shift
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
ZSM-5	zeolite socony mobil-5

1. Introduction

FCCs are used in a well-know process for the conversion of heavy gas oil into gasoline blend compounds. Cracking of big molecules is obtained at around 500 °C by means of a powdered catalyst without hydrogen. Hence, the catalyst is removed and the hydrocarbons are separated into valuable commercial products in the fractionation column. These products are gasoline, fuel oil and LPG. During the FCC process, oil and its vapour at 250–425 °C are injected into the riser reactor, in order to reach the catalyst at a temperature between 680 and 730 °C (Sadeghbeigi, 2000). The injected oil is atomised with steam in order to increase the reaction rate of the cracking process, that takes place at 500–540 °C and 2.5–3.0 bar. Manufacturing techniques are well described in the handbook written by Sadeghbeigi (2000). The fluidised catalyst and vapours are separated in a double cyclone: hence, further oil is removed from the catalyst by stripping with steam. Some catalyst is lost both in the reactor and regenerator, but other fresh catalyst is added. Cracking processes generate coke as a by-product and this reduces its catalytic properties because it collects on the active

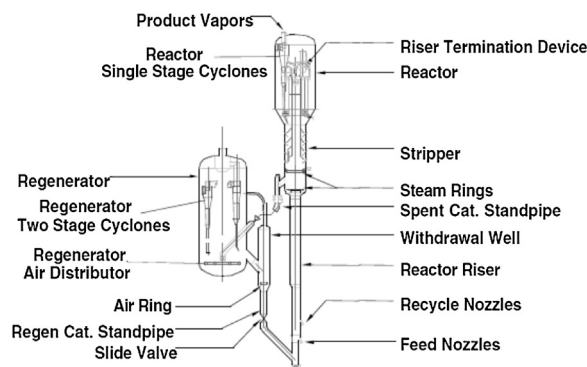


Fig. 1. Reactor–regenerator of modern FCC units (Jones and Pujadó, 2006).

surface. Catalytic cracking units are designed according to the planned frequency and procedure with which FCCs are regenerated (for instance single- or two-stage regeneration). However, over time, deactivation is slow but irreversible due to the high temperature of the process and the presence of poisoning metals like vanadium and nickel. Deactivation of FCC catalysts causes a drop in activity but even in selectivity of the cracking process. Deactivation by cooking is due to site coverage and pore blockage. A first stage of coke formation entails the adsorption of coke precursors on the catalysts surface; thus, a combination of simultaneous reactions leads to the formation of coke. Afterwards, polycyclic aromatics condense from cyclisation of alkyl aromatics: polycyclic aromatics are the main coke precursors. Most acid catalysts enhance the polymerisation of olefins. Catalysts containing rare earth elements promote hydrogen transfer reactions that produce multi-ring aromatic compounds. The FCC unit is shown in Fig. 1.

The quality of the feedstocks also influences coke formation. It was demonstrated that the catalyst has different [Si(nAl)] structures in its fresh, spent and regenerated states. Moreover, there is a progressive loss in crystallinity from fresh to regenerated catalysts, as demonstrated by XRD analysis. Surface area by BET analysis decreases linearly (up to –25%) and it is partially recovered after regeneration. This means less active sites available for catalytic reactions (Behera and Ray, 2009). As regards poisoning by metals, vanadium and nickel are the main poisons. Vanadium is the most dangerous since breaks the zeolite's structure and catalyses dehydrogenation reactions. In fact, in V^{5+} state, vanadium reacts to form H_3VO_4 that has a strong intra- and inter-particle mobility and is able to destroy the zeolite much more effectively than vanadium at lower oxidation states. Nickel has only a dehydrogenation activity, which is less affected by the oxidation state (Wallenstein et al., 2000). Metal deposits onto the catalyst surface are converted to the corresponding oxides during the regeneration process (Gerber et al., 1999). The catalyst, once regenerated, flows back to the reactor riser, where it is cooled by vaporisation of the feedstock and by the heat absorption required for cracking reactions (European Commission, 2013). Feedstocks of the FCC units are usually heavy diesel and VGO from the atmospheric distillation column.

Sulphur, nitrogen, and some metals are the main contaminants of the feed and affect the yield and quality of the product as well as the lifetime of the catalyst. Higher sulphur in the feed is reflected in the products. Nitrogen compounds cause a temporary deactivation of the catalyst, and this lowers the conversion rate. Nevertheless, this effect is reversible and can be controlled by increasing the reactor temperature. As already mentioned, nickel and vanadium cause the most severe problems (Parkash, 2003). Early FCC catalysts were naturally occurring clays, but they had low cracking activity and

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