

THE MANAGEMENT OF SPENT CATALYST IN RCC/FCC UNITS IN ASEAN REFINERIES

by
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I. INTRODUCTION

Catalytic cracking processes convert heavy feedstock (heavy distillate, residue) into gasoline and light cycle stock for middle distillate components. Due to high impurity of feedstock and limited operating condition of catalyst regeneration, fresh catalyst must be added to replace a portion of spent catalyst continuously, to maintain the activity of equilibrium catalyst in the reactor. Spent catalyst must be disposed properly so that it does not cause hazard or environmental concern.

A survey was conducted on the management of spent catalyst in *RCC/FCC* unit in ASEAN refineries as an ASCOPE Technical Committee work programme for 1996. Indonesia was tasked as the Coordinator with the support of Member Countries. The Coordinator for each Member Country is listed in the Table 1.

This paper discusses briefly catalytic cracking process, deactivation of cracking catalyst and the management of spent catalyst in *RCC/FCC* units.

II. CATALYTIC CRACKING PROCESS

A total of about 3,964.0 MBPSD of crude oils are processed in 30 units in ASEAN refineries and 7 units of catalytic cracking processes to convert 296.7 MBPSD of feedstocks (heavy distillate, reduced

crude) into gasoline and light cycle stocks for middle distillate components. These yield a total of about 40 ton/day of spent catalyst.

Residue are very poor quality feed for catalytic cracking. They contain heavy aromatic with Conradson carbon between 3 wt and 8 wt, and metal concentrations of residue increases with the Conradson carbon content (Figure 1). Because of the refractory nature of these heavy aromatics it is difficult to obtain high conversion on some those high aromatic feeds, and the recycle stream containing a high portion of heavy aromatics passes through the reactor virtually unchanged.

Residue feeds tend to have a greater relative tendency toward coke formation than better quality

Table 1
Coordinator of member countries of refinery catalyst

ASEAN countries	Coordinator
Brunei Darussalam	Ms. Lim Jock Hoi Petroleum Unit Jabatan Perdana Menteri
Indonesia	Mr. A.S. Nasution R/D Centre for Oil and Gas Technology "LEMIGAS"
Malaysia	Mr. Yeow Kian Chai Petroleum Nasional Berhad
Philippines	Mr. Benjamin P. Lim POC-Energy Research of Development Center
Singapore	Mr. Hari Haran Singapore Petroleum Co. Ltd.
Thailand	Mr. Suthi Paritpooke Petroleum Authority of Thailand

Program Coordinator of Refinery Catalyst: A.S. Nasution,
Senior Principle Researcher, "LEMIGAS", Indonesia

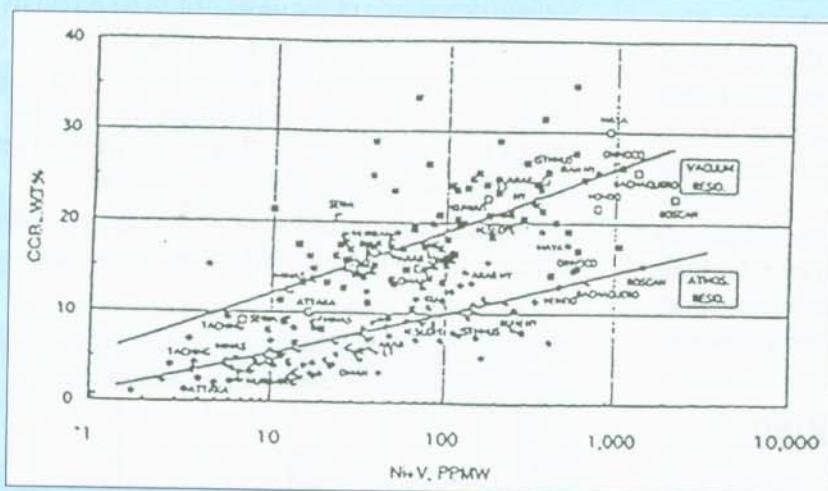


Figure 1
Influence of Conradson carbon content of resid-feed cracking on the metal content

Table 2
Influence of Conradson carbon content of resid-feed cracking on the feed-conversion and product distribution

Conradson carbon, wt %	1.5 - 2.0	2.5 - 3.0	3.5 - 4.0	5.0 - 6.0
Conversion, vol %	82,0	76,8	72,7	66,0
Product distribution				
C ₂ and lighter, wt %	5,2	5,2	6,2	6,4
C ₃ + C ₄ , vol %	28,0	23,0	20,7	21,0
C ₅ + gasoline, vol %	59,8	58,2	55,0	46,0
LCO, vol %	12,5	15,4	18,0	22,0
Slurry, vol %	5,5	7,8	9,3	12,0
Coke, wt %	6,4	6,9	6,9	7,8
Total C ₅ ⁺ liquid, vol %	105,8	104,4	103,0	101,0

Table 3
Influence of metal content of resid-feed cracking on the product distribution

Effective metal, ppm (on Ni)	180	1.130	3.500	
Product distribution				
H ₂ /CH ₄ ratio	in wt	0.7	3.0	10.0
CH ₄ + C ₂ H ₆	% wt	5.8	6.6	7.1
Total C ₄	% vol	14.0	14.0	13.0
Gasoline	% vol	61.0	59.0	54.0
Coke	% wt	2.4	3.1	7.3

feeds such as heavy distillate. Coke selective catalysts generally yield slate, due to impact to higher liquid product yield. Influence of Conradson carbon content of resid-feed cracking on the feed conversion and product distribution of resid cat-cracking is shown in the Table 2. Excessive asphaltene and aromatic contents in the resid feeds are precursors for carbon formation on the catalyst surface which substantially reduces its activity and produces main products of reduced quality.

Vanadium and nickel contaminant results from the volatile porphyrin type components in high boiling fractions of some crude oils. Since contaminant metals (Ni and V) are concentrated in the heavy fractions, higher levels Conradson carbon content of resid-feed cat-cracking generally lead to an increase in the metals level of the equilibrium catalyst; resulting in further degradation of coke and gas yields. Generally, nickel complexes are more refractory than vanadium complexes; and most of the vanadium is deposited on the external surface of the catalyst grain whereas nickel penetrates further inside. This indicates that the asphaltenes are partially hydrogenized on the exterior of the grain before reaching its internal pores.

Hydrodesulfurization of resids with high metal and asphaltene contents does not reduce the catalyst contamination, such the heavy metals and asphaltene concentrate and thus reduce the activity of des-

ulfurization catalyst. Different approaches by refiners have been used for demetalizing the resid feed and improving the cat-cracking catalyst life. Feeds containing 1-2 part per million nickel and vanadium are currently processed in fluid cat-cracking units. Therefore, the trade-off of improved bottoms cracking is significantly poorer coke and gas selectivity (Table 3). This reduces the liquid yield used for high conversion gasoline production. Thus resid cat-cracking gives the high cost of controlling metal contamination of catalyst.

III. DEACTIVATION OF CRACKING CATALYST

Sulphur, basic nitrogen compounds, sodium, nickel, vanadium, iron and copper in the resid feeds act as poisons to cracking catalyst. Sulphur, for instance, has little effect on the present synthetic alumina-silicate catalysts, although it may effect the older natural-clay catalysts, persumably by formation of iron sulfate from iron in the structure.

However, the cracking reaction is inhibited by bases such as nitrogen compounds or alkali. The deactivation by nitrogen compounds is severe, but may be overcome by burning in air in the usual fashion for regeneration. Its effectiveness as poison varies with different nitrogen compounds. More permanent reduction of acidity occurs by depositions of sodium.

Sodium deposition of the order of 1 % wt on catalyst gives no appreciable effects. Loss of activity not only occurs by suppression of acidity, but also by a decrease of surface area. Sodium on the catalyst is known to decrease the stability of the catalyst texture in thermal or hydrothermal treatments.

A permanent deterioration of catalyst performance occurs when metals (nickel, vanadium, iron

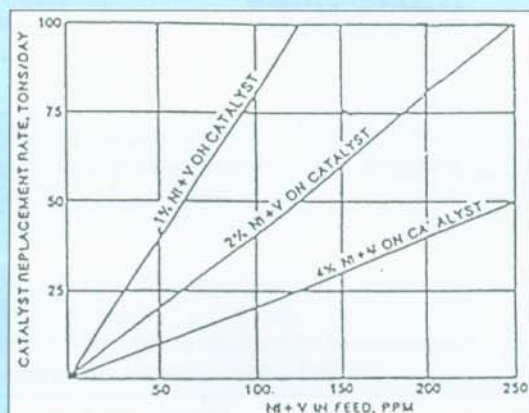


Figure 3
Influence of metal content of resid-feed cracking on the catalyst replacement rate at given metal level of equilibrium catalyst

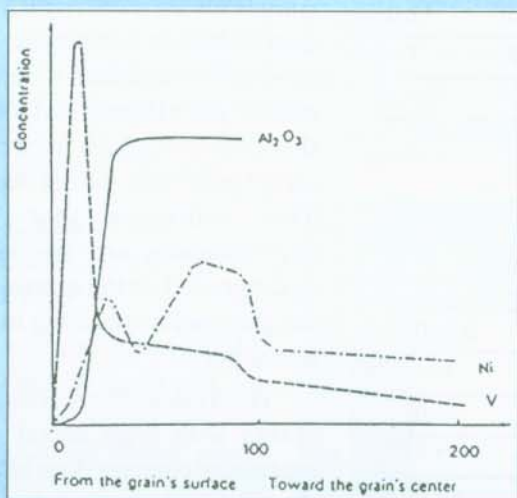


Figure 2
Distribution of Ni and V in the catalyst pores

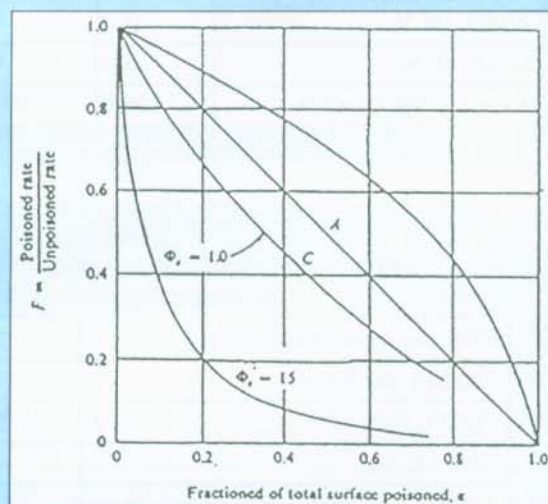


Figure 4
Effectiveness of homogenous and heterogenous poisoned pores by metal deposit

and copper) are deposited on the catalyst. The vanadium is deposited in the form of a film on the outside of the grain (pore mouth poisoning or heterogenous pore poisoning) while nickel penetrates more deeply to inside of grain (uniform poisoning or homogenous pore poisoning), as illustrated in the Figure 2. Heterogenous pore poisoning gives lower pore effectiveness than does the homogenous pore poisoning as shown in the Figure 3.

Although those metals may effect activity by covering active cracking sites, their decreasing pore effectiveness is more important. For this reason, the term "selectivity poison" has been proposed. Accumulation of these metals on the catalyst gives rise to the development of dehydrogenation activity leading to increased formation of gases and coke at the expense of gasoline yield. It can be inferred that nickel is about four times as harmful as vanadium. If the metallic concentrations in the catalyst are expressed in ppm then the effect is a function of: $Cu + Fe + 4V + 14Ni$. If the sum is greater than 1,000 ppm the catalyst is badly contaminated. The results of a catalyst replacement rate using resid feeds with different metal contents are shown in the Figure 4. Metal impurities of spent catalysts in RCC/FCC units is given in the Table 4.

Metal passivation deactivates harmful metal deposited on the cat-cracking catalysts which are responsible for decreased liquid yields and increased hydrogen and coke yields. The treating agent, which is an oil soluble compound containing antimony, deposits contaminant metals on the catalyst and deactivates them into poorer nickel dispersion without deactivating the catalyst. The most important metals that affect on the formation of catalyst coke and hydrogen are nickel, vanadium and iron. It appears that the present of antimony is important. For example, when 0.5% wt antimony was deposited, gasoline yield increased by 14%, coke yield decreased by 22% and hydrogen yield decreased by 57%. For this reason, catalysts with large pores, low surface area matrices would be better for nickel tolerance. However, these catalysts have less than the optimum matrix activity for cracking bottoms and are only appropriate when nickel tolerance is the sole objective.

Vanadium deactivates catalyst by destroying the catalyst zeolite component. Zeolite destruction begins in the regenerator, where the combination of an oxidizing environment, high temperature and steam can form vanadic acid. The acidic attachment causes the zeolite pores to collapse with a loss of surface area and acidity. Since vanadium deactivation is es-

Table 4
Metal Impurities of Spent Catalyst in RCC/FCC Units

No.	Units	ASEAN			Europe (Engelhard catalyst)	USA Ashland Refinery	Australia BP-Kuwana Refinery	
		Indonesia	Thailand					
1.	Catalyst manufacturer	CCIC	CCIC	Grace	Engelhard	Filtrol	CCIC	
2.	Spent catalyst							
2.1	Type	FCC	RCC	FCC	FCC	RCC	RCC	
2.2	Total (1)	ton/day	1.2-2.0	14.0-27.0	1.2-1.6	-	30,0	8.5-1.0
2.3	Metal Impurities							
2.3.1	Nickel	ppm	895	14.850	1,400	2.000	800	7.000
2.3.2	Vanadium	ppm	998	460	3,800	3,00		
2.3.3	Antimony	ppm	-	-	-	1.200	-	-
2.3.4	Copper	ppm	-	-	21	-	-	82
2.3.5	Iron	ppm	2,00	7.800	57.000	-	-	9.230
2.3.6	Sodium	ppm	1.620	4.000	-	-	-	-

⁽¹⁾ - Total spent catalyst about 40 ton/day (included Philippines and Singapore)

Table 5
The management of spent catalyst in RCC/FCC Unit

No.	Disposal method	Units	ASEAN		Europe	USA	Australia	Japan
			Indonesia	Thailand				
1.	Land fill							
1.1	In situ disposal		FCC	-	-	-	-	-
1.2	Ex situ disposal		-	RCC	-	-	clay layer	-
2.	Recovery of spent catalyst							
2.1	Asphalt filler		-	-	-	+	-	-
2.2	Clay filler		-	-	Red Brick	-	-	-
2.3	Cement filler		-	-	-	-	Paving Block (fines)	+
2.4	Cement industry		-	-	-	-	Limited	-
3.	Spent catalyst content	% wt	-	-	5,0	1,5	-	-
4.	Sintering process							
4.1	Temperature	°C	-	-	800	-	-	-
4.2	Time	hour	-	-	24	-	-	-
5.	Metal leaching							
5.1	Nickel	ppm	-	-	0,12	0,003	-	0,10
5.2	Vanadium	ppm	-	-	0,32	0,021	-	0,07
5.3	Antimony	ppm	-	-	-	0,012	-	-

essentially an attachment on the zeolite, a typical approach to improve vanadium tolerance has been addition of basic materials to titrate vanadium. These materials included ally earth metals (Mg, Ca, Sr, Ba), alumina, phosphorus, and barium titanate.

IV. THE MANAGEMENT OF SPENT CATALYST IN RCC/FCC UNITS

The management of spent catalyst in RCC/FCC units and metallic by-products has become increasingly more complex over the last couple of years, due to tightening environmental concern. The management of spent catalyst in RCC/FCC units in ASEAN refineries and others is presented in the Table 5.

In Indonesia, spent catalyst in FCC and RCC units amounting to 1.2-2.0 and 14.0-27.0 tons/day and containing total metal impurities (Ni, V) of 2.000 to 15.000 ppm are disposed to in-situ and ex-situ landfill, respectively. Thailand has 1.2-1.6 tons/day of spent catalyst (FCC) containing about 5.000 ppm of

(Ni, V) content, and this is sent to red brick industry as a clay filler. Spent catalyst/clay ratio of: 5/95 by weight and sintering temperature 80°C in 24 hours are applied

Engelhard spent catalyst in RCC/FCC units in Europe is used as asphalt filler with asphalt content of up to 1.5 percent in the final asphalt product for manufacturing roadbed construction. Spent catalyst of all Japanese refineries RCC/FCC is blended into a raw material for manufacturing concrete blocks, tiles and brick. BP-Kuwana refinery in Australia sent its spent RCC to cement industry for manufacturing pairing block. Almost all United States refinery use landfill containing natural clay layer for disposal of their spent catalysts. They are laid layer by layer with in a medium of spent limestone. The life of this landfill is about 50 years. Outlet to cement manufacturing is limited in United States refineries. In Japan, spent catalyst in RCC/FCC units is mainly blended into a raw material for manufacturing of concrete blocks, tiles, bricks (as filler). Some are being used for steel

manufacturing industry (as heat insulator). Due to the fact that the business of cement manufacturing and road constructions are very active, they would easily be found as the outlet of recycling for these spent catalysts.

Spent RCC/FCC catalyst are also reused as an alternate raw material in the making of stainless steels where spent nickel, for example, is used; further, in the manufacture of metal salts and chemicals. This recycling process keeps thousands of tons of usable materials from being dumped into landfill. Spent RCC/FCC may sometimes have a negative value and cost to be reclaimed. This results from low metal content (compared to spent catalyst of hydroconversion processes), low metal values, and high extraction costs or metal losses. However, the end result is reclamation and recovery which eliminates or reduces landfill.

The micronutrient industry is an example of such an end market. The production of micronutrients involves a simple process. Where metal oxide are blended together, acidulated with sulfuric acid to yield primary metals, granulated, sized, and shipped to fertilizer manufacturer. The micronutrients are then blended with other fertilizer ingredients to correct for regional soil deficiencies.

To maximize the reclamation of spent RCC/FCC both economically and environmentally, five factors should be addressed: (1) proper planning and physical handling; (2) transportation of spent catalysts; (3) environmental concerns; (4) end uses of spent catalyst; and (5) choosing the proper safe reclamation "homes" for the full range of spent catalysts and other metallic by-products. Proper classification of spent catalyst is required prior to reclamation and recycling. Tests should be performed on these spent catalyst to find out whether or not their materials are hazardous waste such as toxic, corrosive, leachable, ignitable.

The most common test for spent catalyst is the toxic characteristic leaching procedure (TCLP). This test determines the leachable hazardous characteristics of a spent catalyst and its metals content. Further, a full chemical analysis should be performed to verify the spent catalyst and its actual content, as well as to determine whether or not a spent catalyst is classified as a nonhazardous or hazardous material, or as a RCRA hazardous waste.

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