

# Effect of Resid Addition to Fluid Catalytic Cracking Feedstocks – Assessment in the Laboratory

a report by

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## The Problem

The decrease in both the quality of crude oil and demand for fuel oil, together with the uncertainty of oil supply in some countries, is contributing to the increasing use of residual feedstocks in refineries. Various commercial processes (e.g. hydrocracking, catalytic cracking and coking) are able to refine such feedstocks. However, the trend is particularly clear in the catalytic cracking of hydrocarbons (fluid catalytic cracking [FCC])<sup>1</sup> due to its versatility and high efficiency in the conversion of high-molecular-weight feedstocks. Moreover, at present some FCC technologies exist that can exclusively process residual feedstocks.

If resids are to be added to conventional vacuum gas oil (VGO) feedstocks, which is a standard operative strategy, it is necessary for refiners to know about their reactivity and expected contribution to the product slate. Usually this matter is not adequately explored, even though it is very important because it can define the economic balance of the whole refinery, the evaluation and selection of catalysts and, consequently, the expected changes in operations.

Resids differ from conventional VGO feedstocks as they have a higher proportion of catalyst contaminant metals such as Ni, V, Na and Fe, of polynuclear aromatics that are strong coke-forming compounds

and of sulphur and nitrogen heteroatom species.<sup>2</sup> Average molecular weights are very high, with boiling points above 530°C. They have high naphthenic, aromatic, resin and asphaltene contents, with an extremely complex chemical structure. As a result, resids have a large Conradson carbon residue (CCR) index above two. This means that the coking potential is high and imposes a number of effective limitations for handling, processing and laboratory evaluation.

## The Experimental Tool

Knowledge about the behaviour of a particular set of resids, VGO, catalysts and operative conditions can be generated in the laboratory.

A method was developed to assess the impact of the addition of resid to conventional FCC feedstocks in a simple and effective manner, based on the use of a batch fluidised bed laboratory reactor named the Chemical Reactor Engineering Centre (CREC) Riser Simulator.<sup>3</sup> This simulator was designed specifically for tackling studies about FCC that mimic the operative conditions of commercial units. Its basic design concept considers that a small slice of an ideal riser, carrying the mixture of catalyst particles and hydrocarbons that 'see' each other while moving along the riser after being put into contact, can be located in a batch reactor with internal recirculation. Thus, the residence time and the position along the ideal riser can be considered analogous to the reaction time in the CREC Riser Simulator.

An impeller rotating at very high speed on top of the CREC Riser Simulator chamber that keeps the catalyst between two metal porous plates induces circulation of the reacting mixture in an upward direction through the chamber, thus fluidising the catalyst (see *Figure 1*). When the reactor reaches the desired experimental condition, the reactant is fed through an injection port. As soon as the reaction time is reached, products are instantly evacuated and sent to analysis.

## Method

The dissolution of very viscous or solid reactants into proper solvents allows them to be processed more easily in the laboratory and can aid the determination of products formed from their conversion. This approach was very useful in identifying the products obtained from polymers recycled into FCC units as a means of decreasing their post-use environmental impact.<sup>4</sup>

This technique can be particularly useful if the solvent is inert, because the products observed would only be formed by the reactant being studied. For example, benzene is essentially inert under FCC conditions and only produces a small amount of coke. Considering that a universal, ideal solvent does not exist, the same approach can be used with other solvents as long as they convert at a low level. In these cases, background experiments with the solvent alone can provide a basis (conversions, product distributions) by which to account for and



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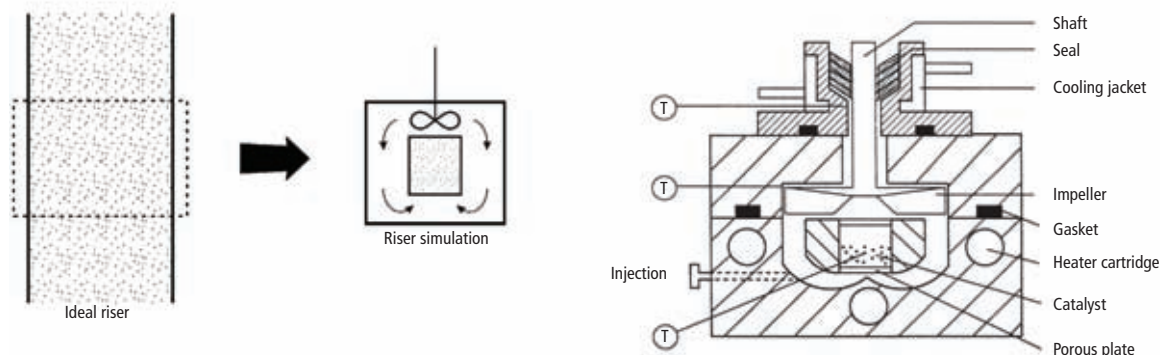


Gabriela de la Puente is a senior researcher at INCAPE, where she works on heterogeneous catalysis and particularly on the catalytic conversion of hydrocarbons. She graduated in Chemistry and holds a PhD degree in Chemistry from the Faculty of Chemical Engineering of the University of Litoral (FIQ, UNL) in Santa Fe, Argentina. She is the author of publications on fluid catalytic cracking, catalyst evaluation, plastic recycling and development of new catalytic processes in

international journals. She is the Director of Studies of Chemistry career at the graduate level in FIQ, UNL and a Professor of Thermodynamics at the graduate and postgraduate levels.

Alejandra Devard holds a degree in Chemistry from the University of Litoral in Santa Fe, Argentina, and she is now a postgraduate student developing a thesis on resid conversion in fluid catalytic cracking, aimed at the study of the reactivity of the various fractions in resids and the feasibility of their conversion into useful petrochemical raw materials. She is the author of four papers on the subject in scientific journals.

Figure 1: Chemical Reactor Engineering Centre Riser Simulator



discount the results of such conversion when the reactant and solvent are present together over the catalyst.<sup>4</sup>

In order to assess conversion and product distribution from a resid, a conventional commercial equilibrium FCC catalyst was used (unit cell size 2.423nm, specific surface area 139m<sup>2</sup>/g, zeolite load 16.9%, rare earth oxides 1.26%, and Albemarle accessibility index<sup>5</sup> [AAI] 5.5). The residual feedstock (see *Table 1* for properties) was an atmospheric tower resid from a naphthenic crude, which was diluted into toluene and methylnaphthalene.<sup>6</sup>

#### Results and Discussion

Careful mass balance calculations in the experiments with reaction times from 10 to 25 seconds allowed assessment of the conversion

and product slate from the resid.<sup>6</sup> It can be observed in *Table 2* for the case of an experiment performed at 550°C that the most significant detail is the high coke yield, as expected. This fact is in line with commercial observations.<sup>7</sup> This is true evidence of the particular contribution of the resid to the product slate when converted under FCC conditions.

The approach was extended to observe the behaviour of mixtures made up of 'real' hydrocarbon cuts and resids and to compare the conventional catalyst used in the development of the method with a resid-type commercial equilibrium catalyst (unit cell size 2.427nm, specific surface area 125m<sup>2</sup>/g, zeolite load 14.8%, rare earth oxides 2.94% and AAI 8.3).<sup>8</sup> In order to facilitate experimental handling and analysis of results, a hydrocarbon cut close to a FCC light cycle oil



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**Table 1: Properties of the Residual Feedstock**

Distillation (% volume)		
Initial point	°C	294.8
5	°C	385.2
10	°C	411.7
20	°C	448.8
30	°C	473.1
40	°C	500.2
Final point	°C	513.9
Yield	%	45.6
Density	g/cm <sup>3</sup>	0.95
Viscosity at 50°C	sSU	350
Iron	ppm	28
Nickel	ppm	15.6
Vanadium	ppm	38.2
Nitrogen	ppm	3336
Sulphur	%	1.4
CCR	%	8.11

CCR = Conradson carbon residue.

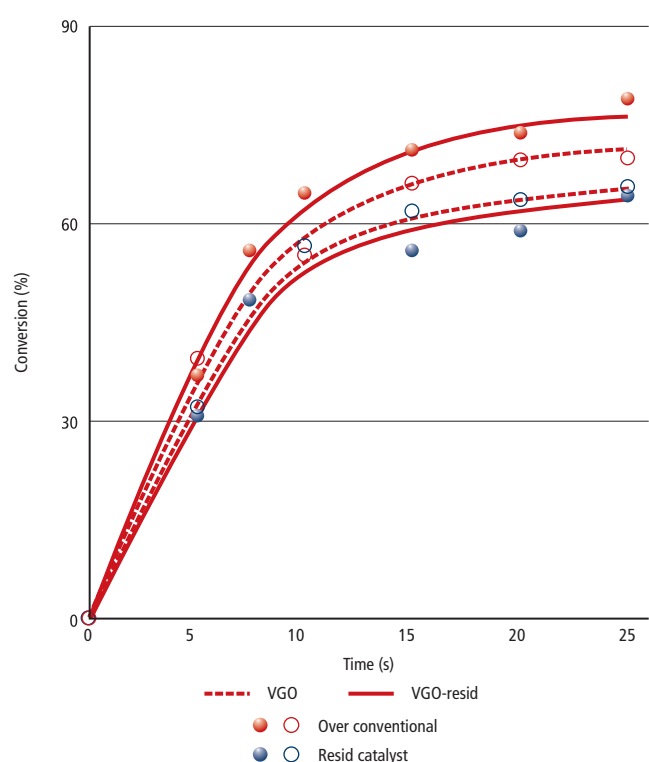
**Table 2: Distribution of Products from Resid Conversion, 550°C, Reaction Time 15 Seconds**

Hydrocarbon group	Yield (%)
Dry gas	3.5
Liquified petroleum gas	23.0
Gasoline	45.5
Light cycle oil	8.5
Coke	13.3

**Table 3: Selectivity to Gasoline and Coke from the Resid, Light Cycle Oil and Their Mixture, 550 °C, Reaction Time 15 Seconds**

Feedstock	Conventional Catalyst			Resid Catalyst		
	LCO	LCO–resid	Resid	LCO	LCO–resid	Resid
Gasoline selectivity (%)	65.9	64.0	53.3	73.2	68.5	57.2
Coke selectivity (%)	9.8	10.5	15.6	7.9	8.1	12.8

LCO = light cycle oil.

**Figure 2: Conversion as a Function of Reaction Time**


VGO = vacuum gas oil.

(LCO), which can represent more complex hydrocarbon mixtures, was used with 10% resid added. This resid proportion, which should not significantly alter the FCC operation, can be considered typical of commercial practice and is aimed at reducing the magnitude of residual streams.

It was observed that the yields of the most important hydrocarbon groups from the resid, the LCO, and their mixture, followed a very similar trend as a function of conversion on a given catalyst. Indeed, at least with this particular set of feeds, the yields seemed to depend on the conversion level alone.

However, some differences in the yields were observed between catalysts as a result of their different formulations (see Table 3). Under the same conditions, the resid catalyst yielded more gasoline than the conventional catalyst when cracking the resid alone, which moderately translated into conversion of the resid–LCO mixture.

The better coke selectivity of the resid catalyst can also be observed. As an example, it can be concluded that the resid catalyst would

Resids differ from conventional vacuum gas oil feedstocks as they have a higher proportion of catalyst contaminant metals

be convenient if the selectivity of gasoline is to be maximised in the refinery when this particular residual cut is to be processed and added to the standard feedstock.

Following this approach, the benefits and problems with the addition of resid were pre-evaluated in the laboratory. Ten per cent of resid was then mixed with a typical VGO (see properties in Table 4) and subjected to the same conversion experiments on the conventional and resid catalysts tested.<sup>9</sup> The conversion profiles as a function of contact time in the CREC Riser Simulator reactor can be observed in Figure 2. The conversions achieved are in the range of usual commercial values.

It is obvious that whatever the feedstock, the conventional catalyst is more active than the resid catalyst. When the resid is included, however, the response of each catalyst is significantly different: the resid catalyst shows the same or slightly lower conversion compared to the VGO alone. By contrast, the conventional catalyst increased conversion by about five points. This could be due to the higher reactivity of a fraction in the resid compared with VGO. This is because some hydrocarbon molecules with high molecular weight could have long aliphatic chains attached to aromatic rings and behave similarly to a more paraffinic, lighter feedstock in FCC. The activity of the resid catalyst would not be enough to show this behaviour with the mixture.

The results were similar to those observed with the resid–LCO mixtures. The yields of the main hydrocarbon groups obtained with both catalysts in the conversion of the VGO, the resid–VGO mixture and the resid

alone showed that, at least under these conditions and catalysts, they followed the same variation as a function of conversion (see *Figure 3* for the example of the resid catalyst).

The characteristics resulting from the different catalyst formulations are revealed in the comparison of various product selectivities. In effect, with both feedstocks (VGO and resid-VGO) the conventional catalyst (more active) produces more dry gas and LPG and less gasoline than the resid catalyst (see *Table 5*). The catalyst designed specifically to convert residual feedstocks shows better coke selectivity, which is crucial.

A very important effect of the addition of this resid to VGO can be observed in the comparison of the gasolines compositions. Changes were more perceptible on the resid catalyst. At typical conversions, when resid was added to VGO, the content of olefins in gasoline increased significantly (from 23.3 to 28.0%), while that of aromatics (from 36.9 to 35.1%) and isoparaffins (from 28.0 to 25.2%) decreased. This was coincident with observations in commercial and fluidised bed laboratory ACE units.<sup>10</sup> Changes in the gasoline composition after adding resid to the VGO followed the same trends on the conventional catalyst, but were only significant at low conversion levels – far from usual refinery values.

These results are consistent with the catalyst properties, because the resid catalyst has a higher accessibility and would adsorb components from the resid more extensively than the conventional catalyst. As a consequence, the higher olefin yields in gasoline would result from the more significant reduction in density of paired sites. This would have a more significant impact on hydrogen transfer, given its dependence on that surface property.<sup>11</sup>

This method is also useful to determine the yields of particular hydrocarbons such as, for example, isobutane or C4–C5 olefins that can be used as raw materials for other processes. It can be seen in *Table 5* that the resid yields more light olefins than the VGO over the two catalysts; however, this fact is again reflected in the conversion of the mixture with the resid catalyst alone.

## Conclusion

The observations about yields, selectivities and group compositions in the experiments with resid or VGO alone, as well as with their mixture, strongly suggest that the impact of resid addition cannot be evaluated with information from the base reactants only. The intended mixture must be analysed.

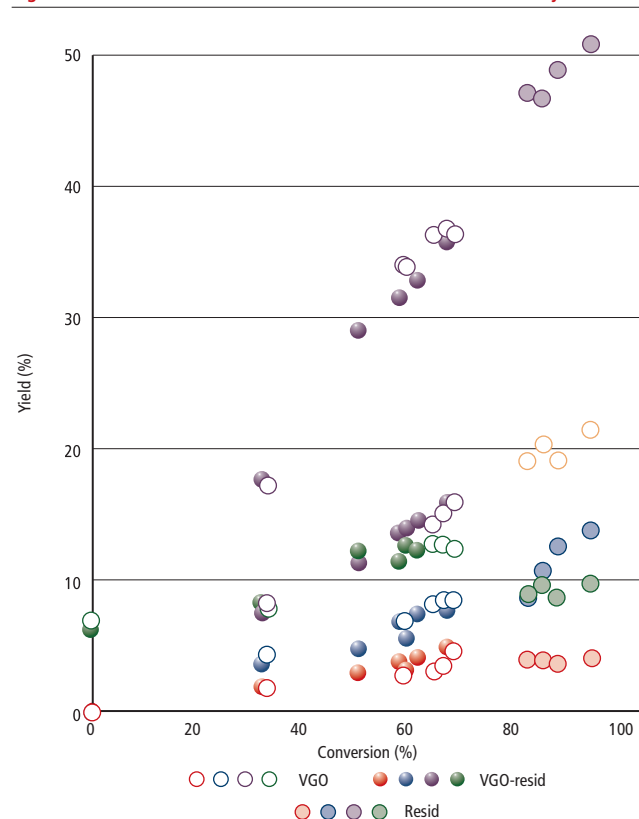
The application of this approach to the evaluation of the performance of commercial and prototype FCC catalysts has produced very satisfactory results. ■

**Table 4: Vacuum Gas Oil Properties**

Distillation (% volume)		
10	°C	361
30	°C	408
50	°C	432
70	°C	456
90	°C	494
Density	g/cm <sup>3</sup>	0.916
° API		22.3
Iron	ppm	2.4
Nickel	ppm	0.1
Vanadium	ppm	0.7
Nitrogen	ppm	1,441
Sulphur	%	2.03
CCR	%	0.11

CCR = Conradson carbon residue.

**Figure 3: Yields as a Function of Conversion Over Resid Catalyst: 550°C**



VGO = vacuum gas oil.

**Table 5: Selectivities from the Resid, Vacuum Gas Oil and their Mixture, 550°C**

Feedstock	Conventional Catalyst			Resid Catalyst		
	VGO	VGO-resid	Resid	VGO	VGO-resid	Resid
Gasoline selectivity (%)	52.4	49.3	53.3	57.6	57.2	57.2
Coke selectivity (%)	13.1	14.7	15.6	13.1	11.6	12.8
C4 olefinicity	0.33	0.34	0.45	0.48	0.51	0.53

VGO = vacuum gas oil.

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