FCC Testing at bench scale: new units, new processes, new feeds.

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Abstract

As the FCC process has evolved over decades, several laboratory scale equipment have appeared to maintain a proper assessment of catalysts activity. Several laboratory equipments are available for simulating the FCC process, from the well known fixed bed, MicroActivity Test to newer, fluid bed or transported bed units. As well, a number of units have been created to simulate other parts of the process such as regenerator or stripper, The increased pressure for treating non-conventional feeds, from reprocessing gasoline to extra-heavy feeds or oils produced from biomass containing large amounts of heteroatoms, increase the needs to have a laboratory test which is as close as possible to the process so that data extraction from the laboratory test are simplified, thus less prone to errors or misunderstanding.

Keywords

Laboratory testing, catalytic cracking, naphtha cracking, coked catalyst, biooil cracking

Highlights

- FCC process is adapting to new feeds and new processes
- Heavy resid feeds and biomass-derived feeds are being extensively tested
- Significant operation and process changes are contemplated to squeeze maximum value from feeds: naphtha reprocessing, use of partially coked catalysts, several independent risers.

1. Introduction

The catalytic cracking process has been and is still one central piece in the refinery in converting the bottom of the barrel into lighter products, from small olefins to middle distillates, with a high profitability derived from limited processing costs. As resources of cheap petroleum crude dwindle, there are increased incentives in treating less conventional, more difficult feeds such as resids and biomass-derived oils. These oils carry a much larger amount of impurities such as Microcarbon, metals, oxygen (among them ketones, aldehydes, acids, furans), nitrogen (pyridines, quinolines, carbazoles), as well as increased amounts of sulphur in resids. For dealing with these problems and avoid being supplanted by coking and/or hydrocracking for the valorization of heavy feeds, catalysts and process development in catalytic cracking will continue [1]

Proper laboratory testing plays a central role in identifying the right catalyst development pathways. For that duty, it is of paramount importance that the data extracted from the laboratory testing can be properly extrapolated to the industrial unit. In the case of catalytic cracking, there is an inherent difficulty due to the coupling of the different operating variables and the extremely fast deactivation of catalyst. This extrapolation is performed through modeling, which complexity will increase together with the differences in operating conditions from laboratory to industrial scale [2, 3]. For example, data extrapolation from a fixed bed will be of increased complexity than from transported bed. For some applications, it is necessary to simulate the effects of reaction-regeneration cycles on the catalyst deactivation, and specific laboratory units and protocols have been developed. A number of laboratory units were developed to simulate the reactor of the FCC unit, from the old but still useful Fixed Bed unit (MicroActivity Test), with its avatar as Fixed Fluid bed, to more recent, transported bed units.

Increased environmental pressure and increased use of cheaper, heavier crudes has put significant pressure on the FCC, as the product slate quality has to be improved using lower quality feeds. In recent years, a number of process developments have been suggested and tested in laboratory units. Gasoline reprocessing has been proposed to lower olefins content and increase propylene production [4,5]. The use of coked catalyst has been claimed to improve coke selectivity and thus enable the use of heavier feeds [6].Another option considered coupling bottoms and naphtha reprocessing in a dedicated, multiple injection point riser to perform simultaneous olefin and diesel yield maximization [7]. These options usually require operating conditions significantly different than routine FCC. Among those, we can highlight higher Catalyst to oil ratio, higher temperatures, and shorter contact time. The

interest on fuels derived from biomass has opened the FCC process to several types of oils produced from biomass such as vegetable oils and pyrolysis oils. The behavior of these feeds usually differ substantially from typical VGO-resid mixture due to the large amount of oxygenates components present in the oils. Finally, heavy resid testing in laboratory may present some challenge due to the higher coking tendency of these feeds and the increased importance of thermal shock between feed and catalyst to reduce coke yield.

2. Laboratory units for testing of catalytic cracking

2.1. Catalytic cracking activity and selectivity assessment

The first step in evaluating an FCC catalyst is to assess its potential in cracking activity and yield selectivity. A number of laboratory units are available for this purpose, and can be classified with the type of catalyst bed and gas flow pattern: fixed bed catalyst and plug flow of gas, fixed fluid bed catalyst and plug flow of gas, fixed fluid bed catalyst and mixed gas, transported bed catalyst and plug flow of gas. The FCC unit operating conditions have evolved over years, from large fluid bed as reactors to short contact time transported bed risers with multiple feed nozzles for high efficiency feed atomization. Conversely, Laboratory tests have evolved, shortening injection time or developing units with transported beds. In the following sections we will describe the different laboratory approximations for testing FCC catalysts, from the point of view of catalyst bed and gas flow pattern.

2.2. Fixed bed catalyst, plug flow gas: Microactivity test

Fixed bed units, which most representative protocol has been normalized in the ASTM D-3907 method, have been used for more than four decades as the most common laboratory test for catalytic cracking. MicroActivity Testing (MAT) main advantage is an extreme simplicity of use. A few grams of pelletized catalyst are necessary, and testing can be carried out in automated units with minimum operation costs [8]. Nevertheless, this protocol has a number of drawbacks that have been widely documented [9]:

- Continuous catalyst deactivation during the test due to coking, while fresh feed is continuously fed to the unit. As a result, the conversion and selectivity of the feed from the beginning to the end of the test may vary substantially. As a result, product distribution is an average of the different product distributions obtained over the duration of the test.

- Coke and temperature profile can appear through the catalyst bed, which changes activity and selectivity during the test, hence the average conversion and product yield. Decreasing bed temperature will also difficult the feed vaporization, increasing

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coke yield. This is especially problematic in the case of resids, which have a large fraction boiling above 500ºC.

- Catalyst is contacted with the feed for a period which can be an order of magnitude longer than in the industrial unit. This leads to increased coke-on-catalysts values.

- Gas residence time is also significantly different than in the commercial unit, as well as temperature history, thus dry gas yield prediction can be largely incorrect.

All these effects sometimes result in inaccurate predictions when the results are extrapolated to commercial unit, resulting in catalyst ranking reversals when compared to pilot plant or commercial unit results. While these deviations can be partially corrected through the use of complex models, this usually increases exponentially the number of parameters and then the associated testing effort for a catalyst evaluation. In the case of new types of catalysts being tested, differences in catalyst deactivation kinetics may lead to misleading evaluation under standard operating conditions. Experimentations at shorter Time-on-stream coupled with the use of kinetic model demonstrated that catalysts with a high deactivation rate such as USY may be outperformed in standard MAT test by new catalyst formulation such as SAPO37, which has lower initial activity but lower deactivation rate [10].

Many laboratories implicated in catalytic cracking testing have developed some variant of the ASTM MAT protocol aimed at improving the reliability of the test. First measures were to use shorter contact time, and improved vaporization of oil through addition of an inert gas as diluents, usually nitrogen [11, 12]. A large effort was undertaken by Grace to improve MAT protocol at the end of 90's, resulting in SCT-MAT (Short Contact Time-MAT). Catalyst bed was diluted and an insert was used to minimize temperature drop and temperature profiles [13, 14]. Reactor internals were modified to minimize dead volumes. Recovery trap was also redesigned to improve test repeatability [15, 16]. Another group also improved performance by optimizing the feed injector material, resulting in less variance in yields and less coke yield when heavy resids were processed [17]. Nevertheless, it can be said that several of the above limitations inherent to the fixed bed catalyst, plug flow gas unit still remain.

2.3. Fixed fluid bed solid, plug flow gas: Advanced Catalytic Experiment (ACE)

Catalytic fixed fluid bed has emerged in the last years as the competitor of MAT test as standard catalytic cracking test. The main difference is that the catalyst bed is fluidized, which eliminates the formation of temperature and coke profiles along the bed. The feed is injected directly into the fluidized catalyst at a regulable height, which allows varying the contact time between feed and catalyst [18]. Nevertheless, the same time averaging effect occurs as

depicted with fixed bed, and catalyst is contacted with feed for a period of time longer than in many fixed bed protocols.

The different hydrodynamics of the two units also leads to some systematic differences in the activity and yields measured in the two units for a given feed-catalyst couple. Reactor modeling [19] has shown that a reactor with a certain degree of backmixing such as fixed fluid bed will favor selectivity toward end-products such as gas and coke against intermediate products (gasoline and LCO) when comparisons are performed at the same space time. Also, the protocol used to perform the testing on the fixed fluid bed has a significant influence on the yields obtained, which may have in turn an influence on catalyst ranking. Indeed, catalyst-to-oil ratio in the test can be modified by changing the catalysts mass, or the amount of feed injected, either by changing feed flow or injection time. Changing conversion through changing time on stream in fixed bed is more an effect of catalyst deactivation rather than the effect of a catalyst to oil ratio calculated as mass of catalyst / over feed injected [20]. Instead, it is recommended the catalyst to oil ratio to be changed through the amount of catalyst used in the bed, while maintaining the volume of the bed constant with the use of diluents.

Because of longer catalyst residence time and differences in hydrodynamics that affect the catalyst deactivation, systematic differences in the results given by fixed and fixed fluid bed protocols have been observed depending on catalysts type. REY catalysts perform better in fixed bed that in fixed fluid bed, while the contrary occurs for USY catalysts [19]. Coke deposition affects faster the whole catalyst bed when it is fluidized [21]. As a consequence, USY catalyst, which has a lower selectivity to coke, performs better in the fixed fluid bed than in the fixed bed.

Both fixed and fluid bed equipments have been shown to provoke ranking reversal compared with pilot plant results [2, 13, 22]. This has prompted the development of reactors that better mimic the catalyst and feed contact in the FCCU riser.

2.4. Fixed fluid bed solid, well mixed gas: Berty type reactors Riser Simulator

Recycle reactors are particularly useful in catalyst evaluations for gas-solid reactions. Its design can be accommodated to achieve similar mass and heat transfer than in commercial operation. In this type of units, an impeller circulates the gas though a central catalysts basket, where the catalyst is confined. The design was adapted to FCC by Kraemer & de Lasa, in an unit called Riser Simulator® [23]. The unit consists of an internal recycle reactor, where a turbine-type impeller, located just above the catalysts basket, produces an upward gas flow through

the catalyst, producing a vigorous fluidization. The solid is retained in its basket by two metallic porous plates [24]. The feed is injected by a heated syringe in the system at the beginning of the test, then the gas mixture is allowed to contact with the catalyst during a short time, typically 2 to 10 seconds. The content of the reaction chamber is then opened to a vacuum-emptied capacity, lowering the pressure of the system to below 0.1 bar, aimed at simulating the stripping step. The contact between the gas phase and catalyst is then similar to a plug flow, and more representative of the contact between solid and feed in the industrial riser-type reactor and fixed (fluid) bed reactors, especially regarding the catalyst and gas residence time [9]. A number of studies in catalysts evaluation [24], kinetic study [25], feed evaluations [26-28] have been carried out with this unit. Pressure monitoring during the tests also allowed for an estimation of adsorption constants of feed and products on the catalyst. Limitations appear for treating heavy feeds due to the need of full vaporization of the feed to be circulated as gas phase though the catalyst, and for the stripping protocol. As happened with fixed fluid bed, systematical differences in catalyst performance were noted between recycle reactor and fixed bed [29].

2.5. Transported bed solid, plug flow gas: Microriser, Microdowner Unit, most pilot plant

Bench scale transported bed reactors have been developed to extend the testing range of laboratory units to below one second catalyst residence time, to test for ultrafast catalytic cracking and explore the deactivation patterns in the very first moments of cracking. It is also another option to fill the gap between small fixed (fluid) bed units and pilot plant, with a contact between solid and hydrocarbons more representative of the industrial riser reactor.

One such design is the MicroRiser® developed and operated by Helmsing et al. At the core of the unit is a bended reactor, of adjustable length (by adding or removing sections) in where the catalyst is pushed through with a large nitrogen flow. The system was designed to ensure a plug flow as perfect as possible through the unit reactor, adjusting catalyst flow rate and nitrogen carrier to avoid backmixing in the reactor bends [30]. As a result, very little dispersion on solid particle residence time is observed, with Peclet numbers above 1000. Note that this is significantly better than in industrial risers, were some degree of backmixing exists, and Peclet numbers of 5 to 16 were measured [32]. The narrow size of the reactor also improves the isothermicity of the reaction. As a consequence, the reactor can be easily modeled through a plug flow, isothermal model, which greatly facilitates kinetic data extraction. In particular, it was shown that the deactivation by coke occurs at a very short time scale [33], as was already suspected [34]. After 0.67 second residence time, it was observed that coke yield barely increased with residence time. Meanwhile, while a significant part of the

conversion was carried out in the very first moments of the reaction, the product slate still evolved considerably after the first 0.67 seconds, indicating that coked catalyst retained a significant activity. Product olefinicity in both gas and gasoline products also showed a notable increase, due to the lower hydrocarbon partial pressure. A number of kinetic studies on aromatic feeds [35], vegetable oil cracking [36], or naphtha cracking [37] have been carried out that will be discussed in greater detail below. Limitations of the unit lies in the large hydrocarbon dilution as a consequence of the need to drag the solid through a bended reactor, and the limited ability to process heavy feeds that does not vaporize properly at FCC reactor temperature.

Another transported bed design is the Microdowner, developed by Corma et al. [38, 39]. In this unit, a preheated catalyst is contacted with a colder feed, just as happens in an FCCU unit. The unit is once through to limit its complexity, and short runs (30-120 seconds) limits the needs of catalyst and feed for each test. The reactor solid flow has been set downwards, which facilitates catalyst flow control and limits backmixing. This unit presents less backmixing than in commercial riser units. Significant effort was dedicated to represent feed injection and mixing, promoting thermal shock between the hot solid and colder hydrocarbons. Also, the feed going through the injector is dispersed using two nitrogen flows to achieve smaller hydrocarbon drops. The design of the reactor head maximizes the contact between feed and hot catalyst, ensuring a better vaporization of the feed. Atmospheric resid with 2-5 wt% Conradson Carbon have been routinely tested while heavier resids, with a maximum content of 17 wt% Conradson Carbon, have been successfully processed in the unit. Another feature of the unit is a very efficient stripping that allows minimizing coke yield. After the short residence time in the reactor, the catalyst particles that exit the reactor spread on a metallic porous plate through which nitrogen flows, so that every catalyst particle is instantaneously stripped once it exits from the reactor, minimizing secondary reactions in the separator. A comparison was carried out between MicroActivity Test, MicroDowner Unit and a pilot plant, DCR design. MAT protocol was ASTM modified, with a Time-on-Stream of 30s. Catalyst residence time in DCR pilot plant was around 2.5 seconds, and ranged from 0.8 to 2 seconds in MicroDowner Unit. Pressure was atmospheric for laboratory testing, and 2 bars for DCR. Results from Table 1 shows that main selectivity was similar between the three units, with a little bit more gasoline and less gas for the transported beds. The main difference lied in the hydrogen transfer, as shown in Figure 1 where the differences in isobutene / isobutene ratio, and coke-on-catalyst are pictured. On these items, MicroDowner unit was able to fit DCR data, working at same temperature, a similar (somewhat higher) catalyst to oil ratio and similar residence time in reactor. Other studies including naphtha cracking [40-41], use of

coked catalyst [42] and cracking of oxygenated feeds [43] also have been carried out and will be further discussed below.

2.6. Others aspects of the FCC process: catalyst deactivation; regenerator, stripper simulation

While the assessment of cracking activity is the main driver for FCC catalyst testing, others aspects also have to be simulated. In particular, catalyst irreversible deactivation through high temperature steaming in the regenerator (where the catalyst will spend the majority of its life) considerably affects the resulting cracking activity. While the mechanisms of deactivation are reasonably understood, its simulation by a convenient laboratory protocol is not trivial. The simplest protocol consists in an accelerated steaming with higher steam partial pressure and higher temperature than in the FCC. 100% steam and temperatures ranging from 750 to 816ºC, with some hours of treatment, are among the most common protocols. In some refinements, a portion of fresh catalyst is added to the steamed one, to simulate the continuous catalyst makeup. While it provides a basic standard for catalyst screening, it was shown that metal build-up (especially Ni and V, but also Fe, Na) also plays a significant role in catalyst irreversible deactivation. Wet impregnation with metals precursors is a simple methodology but sometimes gives unrealistic results. Thus, a deactivation protocol based on performing a number of reduction oxidation cycles (corresponding to cracking reaction followed by coke burning in regenerator) was developed, resulting in Cyclic Deactivation Units [44-45]. In these units, the fresh catalyst is submitted to 30+ cycles consisting of reaction with an oil that may be metal-enriched, followed by high temperature regeneration(>700ºC) in the presence of steam. In some alternative protocol, propene is used as reducing agent during the reaction step, resulting in the Cyclic Propene Deactivation protocol. The resulting deactivation of fresh catalyst, and especially ranking of catalyst based on resistance to deactivation, is much better predicted. Also, proper testing protocols based on cyclic steaming have been proved essential for assessing the correct deactivation pattern of SO_x reduction additives in the regenerator [46].

3. Unconventional feeds and process from the point of view of laboratory testing

3.1. Naphtha cracking and high severity cracking

The high demand in olefins and especially propylene has popularized the use of ZSM5 zeolite, which reduces naphtha yield and boost light olefins yields. Yet the use of ZSM5 as co-catalyst is

limited in the FCC, and in order to boost further the light olefins yield, it has been proposed to reprocess the cracked gasoline [4, 5, 47]. This also may have the advantage of shifting significantly the naphtha composition and in particular reducing the amount of olefins, which increases gasoline instability and increases automotive emissions toxicity as olefins are more reactive in the formation of smog. The naphtha stream can be reprocessed either in the same riser or in a parallel, dedicated riser, taking advantage of customized operating conditions. Studies in Riser Simulator [48], Microriser [37] and Microdowner [40-41] have been realized, giving similar results. As expected, olefins, especially longer olefins (7 or more carbons) are considerably reduced in the remaining gasoline. Naphthenes are also cracked to a certain extent, with increasing conversion with the number of carbons in chain. isoparaffins and aromatics yield globally increases, but within class, smaller molecules yield tended to increase yield and longer molecules to decrease yield. The remaining gasoline presented significant increases in isoparaffins and aromatics, resulting in Octane number increase. The mechanisms behind compositional changes are well known, and the resulting composition will depend on the competition between cracking and hydrogen transfer reaction, which in turn will be influenced by the operation temperature. Due to their high reactivity, longer olefins will be cracked readily, whatever the cracking temperature. Yet at stripper temperature and longer residence time, hydrogen transfer will predominate, yielding less LPG olefins and preserving gasoline yield. Higher temperatures will be required to significantly shift the product distribution to LPG olefins. Such higher temperatures may be achieved in a dedicated riser working with higher catalyst to toil ratio, or injecting naphtha before the main VGO injection. The Table below gives an example of the range of yields attainable by reprocessing FCC naphtha under a variety of conditions, which will be dictated by the injection location. High catalyst to oil ratio and temperature may be achieved by injection before VGO, promoting light olefins production, while softer conditions as injection in stripper under moderate temperature and longer contact time will favor hydrogen transfer and hence gasoline yield. Note that under FCC riser conditions, straight run naphtha, composed mainly of parrafins, will not crack significantly [41]. Higher temperature (above600ºC), much longer residence time (as in old fluid bed catalytic crackers) or large amounts of dedicated catalyst such as ZSM-5 will be necessary to achieve high LSR naphtha conversion.

3.2. Using coked catalysts

A number of patents have disclosed the use of partially coked catalyst for improving selectivity to distillate [49] or increase the selectivity towards light olefins, for example in the reprocessing of cracked naphtha [6].

Studies were carried out in different laboratory units (MAT [50], Riser Simulator [51], Microriser [33], MicroDowner [42], pilot plant [52]), which all showed that the cracking catalyst was able to retained a large part of its activity with coke-on-catalyst values ranging from 0.3 to 1.2 wt%. Activity decrease with coke-on-catalyst depends on catalyst, but typically catalyst activity would be divided by two with a coke-on-catalyst (before reaction) between 0.5 and 1 wt%.

Selectivity changes were somewhat different depending on the reactor configuration. Against coke-on-catalyst (and operating at same catalyst to oil ratio), the same tendencies were observed in all units: decrease in conversion, which logically resulted in an increase in gasoline selectivity and decrease of coke and gas selectivity. However, when compared at same conversion (and correspondingly higher catalyst-to-oil ratio), it was observed in fixed bed that gasoline and coke selectivity decreased slightly with increasing coke on catalyst, while gas selectivity increased. In transported bed and recycle reactors, however, hardly any influence of coke-on-catalyst on the main selectivity was observed. Mixture of coked and regenerated catalysts also tended to act as physical mixtures of catalysts with different activity. Product quality, however, was significantly affected, and in particular the olefinicity of the products. Isobutene to isobutane ratio increased significantly in all units, showing that hydrogen transfer reactions were more impacted than cracking reactions, as a result of a decrease in site density by coking. In gasoline fraction, selectivity to olefins also increased at the cost of paraffins. This difference in deactivation rate between the two major reactions implied in catalytic c racking may also explain the differences observed between laboratory units in term of main product selectivity. In fixed bed, where hydrogen transfer reactions role in magnified and higher levels of coke-on-catalyst are obtained and deactivation is higher, more gasoline-range olefins are cracked into LPG olefins, with the observed consequences on selectivity. Meanwhile, in transported bed units, hydrogen transfer is much less prominent, and selectivity mainly impacted by cracking reactions, resulting in nearly invisible selectivity changes. Note that this is no longer true with catalyst which deactivation is much lower and have very low hydrogen transfer activity, such as ZSM5 zeolite additive. In this case, a slight selectivity change in main products was observed, with higher gas yield (mainly olefins) and lower gasoline yield. Sulfur reduction in product may also be affected by coke-on-catalyst, but for a different reason. It was shown [53] that the oxidation state of metals deposited on the catalyst could have a

significant impact on desulphuration. Then, coked catalyst carrying more reduced metals resulted in lower sulfur reduction in gasoline.

3.3. Heavy feeds and resid processing

Resid feeds have been long used in FCC, but have been proved challenging for testing in laboratory. Compared with standard Vacuum gasoils, resids contain larger amounts of contaminants: non-distillable material (Conradson Carbon), metal, sulphur and nitrogen, resulting, among others, in higher coke yields and higher metal load on catalyst. This prompted catalysts developments to improve coke selectivity and mitigate metal detrimental effects, such as active matrices, based for example on alumina.

Fixed bed testing, although useful for catalyst screening, tends to produce excessively high coke yields with resids, especially in the presence of active matrix [54]. As a result, sometimes catalysts designed for resid testing appeared to perform poorly in fixed bed, yielding more coke and less naphtha than more conventional catalysts. However, in pilot plants, resid catalyst exhibited better performance, producing less coke and more naphtha. This effect was related with the different time scale for coke build-up on the zeolite and the active matrix. While the zeolite coking is fast, resulting deactivation similar at short and longer residence time, coke on active matrix changes significantly from short to long residence time, resulting in higher deactivation in fixed bed and poorer apparent performance. Other aspects of testing, such as injector design, also influence fixed bed performance. Improved nozzle material allowed reducing coke yield and yield scatter [17].

Alternative testing protocol for resids was developed in Riser Simulator. In order to improve feed vaporization, resid is diluted in low conversion solvent such as toluene or methylnaphthalene, and resid cracking yields are calculated deducing solvent cracking yields from the cracking yields of the mixture [27]. Mixtures of VGO and Atmospheric resid (10 wt% resid) also have been tested, and showed a good correlation between mixture and pure resid (in solvent) yields [28]. It was also consistently observed that resid cracking catalyst had lower activity than conventional catalyst, but improved coke selectivity, and that resid tended to yield higher conversions than VGO [55] in laboratory units, due to higher coke yield. As in fixed fluid bed unit, it was also observed that the resid cracking yielded more olefinic and less aromatic products.

Unconventional, extra-heavy crudes contains even much larger amounts of contaminants of all types, and will exacerbate further all the issues related to resids. Short residence time and proper feed injection (feed atomization through dilution with inert gas and thermal shock) will prove essential to provide better assessment of the reactivity on such

feeds. Microdowner unit has been successfully run with high CCR resids and extra-heavy crudes, with Conradson up to 17 wt%. Coke yields with atmospheric resids up to 8 wt% were maintained at 10-11 wt% at 70wt% MAT conversion.

3.4. Oils from biomass and opportunity stocks

In order to reduce carbon emissions, a number of feeds from renewable origins are being considered for catalytic cracking to replace part of the traditional VGO/resid. These feeds belong to two main classes: triglyceride-based oils (vegetable oils, tallow, animal fats) and pyrolysis-derived oils (slow or fat pyrolysis, from wood or municipal waste). These feeds are characterized by their large amount of oxygen in form of esters from triglycerides or furans, ketones and phenols, acids in pyrolysis oils [56]. Some pyrolysis oils may also carry significant amounts of nitrogenated compounds such as nitriles and pyridines, and are not recommended for processing in FCC without pretreatment, as the high poisoning effect of such compounds is well known [57-58]

Triglycerides processing did not pose specific problems in testing, being readily miscible in petroleum oils and lacking contaminants such as Conradson Carbon, metals, sulphur. It also has a relatively low content in oxygen, bound in the form of acid functions that are easier to remove [59]. A variety of catalysts were tested in fixed bed, from Y and ZSM5 zeolite to mesoporous materials such as MCM41 [60-63]. In any configuration, these oils could be transformed with a very high conversion into hydrocarbons, mainly gasoline and gases, while the oxygen was removed in form of water and carbon dioxide plus traces of carbon monoxide. Selectivity to gasoline between 45 and 60% could be obtained on Y zeolite, with little diesel, no bottoms and low coke yields typical of light, highly paraffinic VGO. Using smaller pore (ZSM5) or mesopore (MCM-41) catalysts allowed modulating gasoline yield in favor of gas or diesel respectively [60]. Yet it is difficult to obtain very high yields of diesel in a cracking process due to its intrinsic chemistry, and triglycerides catalytic cracking will always be essentially oriented to gasoline and gas production. Gasoline product was found to be aromatic, but the degree of aromaticity, and to a certain extent the gasoline yield, was influenced by the number of insaturations in the oil. More instaurations gave slightly more gasoline with significantly higher aromatic content. Glycerol moiety from triglyceride cracking may be transformed into a range of oxygenated products, including high yields of acrolein [43]. The cracking mechanism of triglycerides was studied in the Microriser® reactor [36] at short contact time. Triglycerides are first converted mainly to fatty acids through an extremely fast thermal process at reactor temperatures of 450-550ºC. The fatty acids are then cracked into

hydrocarbons. The acid function may be removed by decarboxylation. The remaining carbenium ion may then be cracked into smaller olefinic fragments in gasoline and gas range. If the carbenium ion was generated from insaturated fatty acids, it will also present some double bond in the hydrocarbon chain. As a consequence, this carbenium will be more prone to intra-cyclization, yielding more aromatics in the gasoline range and less olefinic fragments in gas range. This corresponds well to the yields differences observed in the cracking of, for example, palmitic or stearic acid (saturated) and oleic acid (insaturated). Higher aromatic gasoline was also correlated with higher coke yield, just as happens with petroleum VGO.

Pyrolysis oils are complex mixtures of oxygenated components, mainly acids, furans, ketones, aldehydes, alcohols and phenols, but also sugars derivates and oligomers. Composition may vary significantly depending on the biomass and conversion process. Oxygen content can be as high as 40wt%, including water content of 15 to 30wt%. As a result, pyrolysis oil has a low heating value compared to petroleum feeds, and mix poorly with the latter. All these properties make the direct co-processing of untreated pyrolysis oil in standard refinery units problematic [64]. For cracking pyrolysis oil in a standalone process, it was rapidly recognized that significantly better results were obtained on medium pore zeolite catalysts such as ZSM5 than on large pore zeolite such as Y or beta or on silica-alumina, because smaller pores decreases the formation of coke from the biooil [65]. Yet the coke yield remained high, and the liquid cracked product, although lower in oxygen, was still considered of low quality with high concentration of aromatics and phenolics [66]. The different component classes found in pyrolysis oil have exhibited very different reactivity and selectivity on ZSM5 catalyst [67-68]. Alcohols will dehydrate rapidly under catalytic cracking operating conditions, giving small olefins. Ketones are less reactive, and are converted into small olefins, aromatics and coke. Acetic acid began to react significantly above 400ºC, and was transformed into acetone that further cracked. Acetaldehyde was found to have a low reactivity, with high selectivity to coke. Several studies [69-71] have shown that small quantities of small oxygenates molecules such as acetic acid, hydroxyacetone, glycerol, could be co-processed with Vacuum Gasoil without drastic changes in product selectivity. Little coke yield increase could be observed, indicating either that competitive adsorption was more favorable to high boiling point hydrocarbons or that hydrogen transfer reactions influenced conversion pathway. Indeed, when co-processed with VGO, acetic acid main reaction products were fuel gas, some LPG and CO/CO_2. Phenol was converted mainly to benzene and water. Oxygenates were found to have more effect on ZSM5 additive, reducing its effectiveness as LPG olefin booster [70].

In order to improve processability of biooils in the refinery and /or mixing with automotive fuels, a significant upgrading would be desirable. While the pyrolysis oil can be

fully deoxygenated through hydrotreating, this required two stage hydrotreatment, it was subjected to strong catalyst deactivation, and resulted in low liquid yield as well as high hydrogen consumption [72]. Another option consists of a partial upgrading of the oil under much softer conditions, either through hydrotreatment or thermal treatment. This partially upgraded oil can then be processed easier in the FCC unit [64, 73, 74]. Significant interactions between biooil and the petroleum stream have been observed, and were attributed to hydrogen transfer reactions. As a result, coke yield from co-processing the mixtures were found to be close to that of processing the hydrocarbon stream alone, while significantly higher coke yields were obtained by treating the upgraded pyrolysis oil in a standalone process. Phenols content in the gasoline obtained from co-processing was also significantly lower than calculated from standalone pyrolysis oil cracking.

4. Conclusions

FCC process and FCC catalyst and feed testing will remain an area of intense activity to face the new challenges of producing cleaner fuels form heavier or unconventional feedstocks. While virtually all refiner or catalyst producer possess a laboratory protocol for catalyst evaluation, it generally rely on fixed or fixed fluid bed testing, which may be less accurate for feed assessment under realistic conditions, especially regarding coke behavior for unconventional feeds. There is then still a gap to be filled for an easily operated laboratory scale unit able to produce cracking data under operating conditions closer to the industrial plant, especially regarding catalyst to oil ratio and residence time. The introduction of a Microdowner unit has represented an important step forward for more realistic laboratory testing, while processing a large variety of feeds with emphasis in heavier and opportunity crudes.

Catalyst developments, but also process evolution, will help the FCC process to adapt product slate. New processing options such as naphtha reprocessing or use of coked catalyst needs proper simulation, especially regarding the use of high catalyst to oil ratio, higher temperature and short catalyst residence time. Finally, the use of biomass-based feeds, often locally produced with a large variability in feed specifications from a location to another one, will also generate additional testing needs.

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Table 1. Comparison between MD (solid residence time in reactor of 0.8 and 2s) with MAT and DCR at 75% conversion. Trx = 550ºC.

	DCR	MAT	MD (0.8s)	MD (2.0s)
WHSV (h^{-1})	195	22	257	203
Solid residence time (s)	2.4	30	0.8	2.0
CTO	7.7	5.45	17.5	8.85
Conversion	75.5	75.5	75.5	75.2
Yields				
Dry gas	4.5	3.2	2.2	3.6
LPG	19.8	20.7	21.2	17.6
Gasoline	46.5	43.3	46.4	49.5
LCO	14.3	15.4	13.4	15.5
HCO	10.2	9.1	11.1	9.3
Coke	4.6	8.0	5.8	4.5
i-C$_4^=$/iC$_4$	*0.95*	*0.17*	*0.68*	*1.14*
Coke on catalyst	*0.59*	*1.23*	*0.33*	*0.51*

Figure captions:

Figure 1. Isobutene / isobutene ration and coke-on catalyt in three catalyst testing units: MAT (+); MicroDowner Unit (◯)and DCR FCC pilot plant (▢). Data at 550ºC.

Figure 1.