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Colegio de Ciencias e Ingenierías, Politécnico

**CONSIDERATIONS DURING THE DESIGN AND
OPERATION OF LABORATORY REACTORS FOR
CATALYTIC CRACKING AND PYROLYSIS, CO-
PROCESSING AND HYDROPROCESSING – A
SYSTEMATIC LITERATURE REVIEW**

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Ingeniería Química

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RESUMEN

Las reacciones químicas catalíticas se estudian a escala de laboratorio variando el diseño de su reactor, sus condiciones de operación, o el tipo y cantidad de catalizador empleado. En este artículo, se presentan las consideraciones durante el diseño y operación de reactores de laboratorio para reacciones de craqueo catalítico, pirólisis, coprocesamiento e hidroprocesamiento, a través de una revisión sistemática de la literatura (SLR) de los artículos publicados en los últimos 5 años relacionados con el tema. Este SLR se llevó a cabo en base a la metodología de ítems PRISMA y SLR de ingeniería. Según los resultados, los reactores de lecho fijo de laboratorio se emplean principalmente para estudios de hidroprocesamiento y la mayoría de los reactores de lecho fluidizado a escala de laboratorio se utilizan para evaluaciones de craqueo catalítico. En referencia a las condiciones de funcionamiento; la mayoría de las reacciones se realizaron a una temperatura de 400-550 °C y presiones atmosféricas. E-Cat y HZSM-5 fueron los catalizadores más comunes empleados para las evaluaciones de reacciones de craqueo catalítico, pirólisis, coprocesamiento e hidroprocesamiento. La tendencia futura en el diseño de reactores catalíticos es la incorporación de nueva tecnología para las etapas de mezcla, calentamiento y alimentación.

Palabras clave: reactor catalítico de laboratorio, craqueo catalítico, pirólisis catalítica, coprocesamiento, hidroprocesamiento.

ABSTRACT

The catalytic chemical reactions are studied at laboratory scale by varying its reactor design, its operating conditions, or type and quantity of catalyst employed. In this study, considerations during the design and operation of laboratory reactors for catalytic cracking, pyrolysis, co-processing and hydroprocessing reactions are presented through a systematic literature review (SLR) of all related articles from the last 5 years. This SLR was carried out based on the PRISMA items methodology and engineering SLRs. According to the results, laboratory fixed-bed reactors are mainly employed for hydroprocessing studies, and most lab-scale fluidized-bed reactors are used for catalytic cracking evaluations. In reference with the operating conditions; the majority of the reactions were performed at a temperature of 400-550 °C and atmospheric pressures. E-Cat and HZSM-5 were the most common catalysts employed for the evaluations of catalytic cracking, pyrolysis, co-processing and hydroprocessing reactions. The future tendency in catalytic reactor design is to include new technologies for the mixing, heating and feeding stages. As coming work, it is expected to use this paper to design and build a novel and useful laboratory catalytic reactor for the studies that are carried out in some investigations. **Key words:** laboratory catalytic reactor, catalytic cracking, catalytic pyrolysis, co-processing, hydroprocessing.

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INTRODUCTION

In the last 5 years, over 100 articles were published on the design and operation of laboratory catalytic reactors. When designing a chemical process, it is necessary to evaluate and describe it on a laboratory scale in order to have a better understanding of its characteristics and behavior [1], [2]. Therefore, laboratory reactors are mainly used for measuring reaction rates and kinetic parameters at diverse temperature and pressure conditions; with a wide range of purposes such as determining the activity, selectivity and catalysts lifespan [3], [4]. In order to optimize catalytic processes, laboratory units are also used for understanding the fundamental chemical reaction, studying heat and mass transfer limitations, modeling the reaction process, scaling-up reactors and validating theoretical models [5].

The design and application of reactors is a complex field that includes several aspects of Chemical Engineering [6]. However, the most common criteria for the selection of reactors are the size and type of reactor, as well as the mode of operation, either batch or continuous. Catalysts development go hand in hand with reactor design, since the reactor will define the contact form and time between the catalysts and the reacting medium. Therefore, if the intention is to perform catalytic reactions, it is necessary to know the suitable reactor design for the specific desired application. Catalytic reactor designers focus on ensuring that the reaction eases the generation of the principal product with the highest efficiency and maximum possible yield [6]–[9]. Moreover, designing a catalytic reactor also considers the best way to minimize purchase and operation expenses; including energy input and removal, or reactants feed [10].

Catalysis is involved in the processing of over 80% of all manufactured products worldwide. Catalytic reactions provide an alternative reaction mechanism with lower activation energy, lower operating temperatures, and a better control over selectivity, increasing the viability and economics of many transformation processes [11]–[13]. Furthermore, a large number

of important chemical and biological processes would not be suitable without the presence of catalysts. To date, the most studied catalytic processes are cracking and pyrolysis reactions; the former being one of the largest applications of catalysis worldwide [14], [15]. Catalytic cracking aims to convert, in a single pass, more than 50% of the feedstock into gasoline and lower boiling products, which could be used as fuels or building blocks for chemical processes [15]. Catalytic cracking is a process that consists of many simultaneous reactions; like C-C bond cleavage of paraffins, dealkylation, isomerization and condensation. It is usually carried out using solid acid catalysts such as aluminosilicates and zeolites [16]. Catalytic cracking is a versatile chemical process applied to a variety of feedstock ranging from gas to heavy oil, being the most common the following: (1) straight-run gas oil, (2) vacuum gas oil, (3) atmospheric residuum, and (4) vacuum residuum, among other crude oil residues or blends of more than one feedstock [17]. In the last decade, residual hydrocarbon cuts such as atmospheric tower bottoms (ATR), deasphalted oil or aromatic extracts were added to the conventional catalytic cracking feedstock [18]. Lately, some blends like heavy oil, extra heavy oil, tar sand bitumen, conversion of low-cost vacuum gasoil, bio-oils and biomass cracking have been added to the feedstock mentioned before in FCC laboratory tests [3], [18]–[24].

On the other hand, the term catalytic pyrolysis is applied for direct thermochemical liquefaction of biomass, various waste materials (plastics, tyres, etc), and microalgae [7], [12], [25]–[27]. Catalysts in pyrolysis influence the yield of bio-oil with a higher calorific value, H/C ratio, and decrease the production of sulfur containing compounds and of oxygenated species compared with the non-catalytic pyrolysis [12], [28]. The main purpose of the process is to convert biomass-derived oxygenates into aromatic hydrocarbons. Liquid, solid and gaseous products obtained, can be used as biofuels or green chemical feedstock. Catalysts can be incorporated in situ or ex situ into a fast pyrolysis system [26]. Despite of the great effort researchers have dedicated into the process; catalytic pyrolysis has not been

developed in commercial-scale yet due to some barriers found. The crucial limit for the up-scaling is the low liquid hydrocarbon product yield and the high coke formation [26]. Catalysts lifetime and regeneration is another limitation of the process [13].

Co-processing allows the combination of diverse bio- and fossil-based feedstock fractions and is found generally under the term of cracking. Fossil-based fractions favorable for this process are straight run gasoil (SRGO), straight run diesel (also called light atmospheric gasoil, LAGO), heavy atmospheric gasoil (HAGO), and heavy vacuum gasoil (HVGO). Bio-based feedstock include lipids that appear in vegetable oils, waste oils or animal fats. Also, edible oils, non-edible oils, residual oils, and pyrolysis bio-oils are of great interest for co-processing [13], [15], [29]–[34]. Hydroprocessing is a traditional refining technology that upgrades petroleum distillate fractions. The two types of hydroprocessing technologies are catalytic hydrotreating (HDT) and catalytic hydrocracking (HDC) [29].

In this context, this study aims to present a compilation of reports from the last 5 years about the design of different laboratory reactors that have been used for the investigation of catalytic cracking and pyrolysis, co-processing, and hydroprocessing reactions. The parameters analyzed and compared during this review are the reactor dimensions, its operating conditions, and finally feedstock and catalysts used as well as products obtained.

REVIEW METHODOLOGY

This systematic literature review (SLR) was carried out based on the Preferred Reporting Items for Systematic Reviews and Meta-Analysis (PRISMA) methodology [35] and the procedure proposed by Kitchenham et al. [36] and Torres et al. [37] who divided the process into three main parts: planning, conducting, and reporting the review. Four stages were completed when conducting the review: identification, screening, eligibility and inclusion of the articles [38]. This research started with the recognition of the universal current state of

the problem, in this case the selection of a catalytic laboratory reactor, and stating the research question. Then, an early investigation was conducted to search existing related Systematic Literature Reviews. As no SLRs were found, the review protocol was performed using a mind map tool. In the mind map all relevant information regarding the methodology was specified as: selected journal search engines, inclusion and exclusion criteria for articles, possible search terms, and the preliminary structure of the final report (see **¡Error! No se encuentra el origen de la referencia.**). Defined literature search engines were ACS Publications, Scopus, Science Direct, and Springer. The definitive search-string was: *"catalytic cracking" AND ("laboratory unit" OR "laboratory system" OR "laboratory reactor") AND design*. The review was restricted to research and review articles, discarding book chapters. Also, the articles were limited to being published in the last 5 years (2015-2020) and written in English.

Retrieved articles information were documented in a table format in Microsoft Excel. The tabulation was performed considering the most important information of the article that contributes with the objective of this review, such as: process described, type of reactor used with its characteristics and operating conditions, type and quantity of catalysts employed, and the products obtained. Articles were fully read and the criteria used for retaining or discarding an article was whether it described a catalytic process and its reactor. Then, the articles were collected in Mendeley reference manager software. Furthermore, articles were classified statistically according to the type of reactor it described (fixed or fluidized bed), and the process it was employed for (pyrolysis, cracking or combined). The reporting stage was elaborated based on the PRISMA Statement 27-item checklist [39]. All this process can be retraced in **¡Error! No se encuentra el origen de la referencia.**

RESULTS AND DISCUSSION

General Approach

After defining the methodological details, 73 articles were retrieved from the definitive search procedure carried out on August 13th, 2020, as illustrated in Figure 1. Additionally, 52 of the cited articles in those documents gave the reactor description, so they were retrieved and also used for this Systematic Literature Review. From all the retrieved articles, 42% were discarded because they did not meet the eligibility criteria, 28% mentioned fluidized-bed reactors, other 24% employed fixed-bed reactors, and 6% of the studies were carried out in combined units. Concerning the fixed-bed reactors, 31% of the articles described hydroprocesses, 24% cracking processes, 24% pyrolysis and 21% co-processing. While 49%, 31% and 20% of fluidized-bed's articles described cracking, pyrolysis and co-processing, respectively (Table 1). It is worth mentioning that just 27% of the studies retrieved, specified the reactor dimensions; which are summarized in **¡Error! No se encuentra el origen de la referencia..**

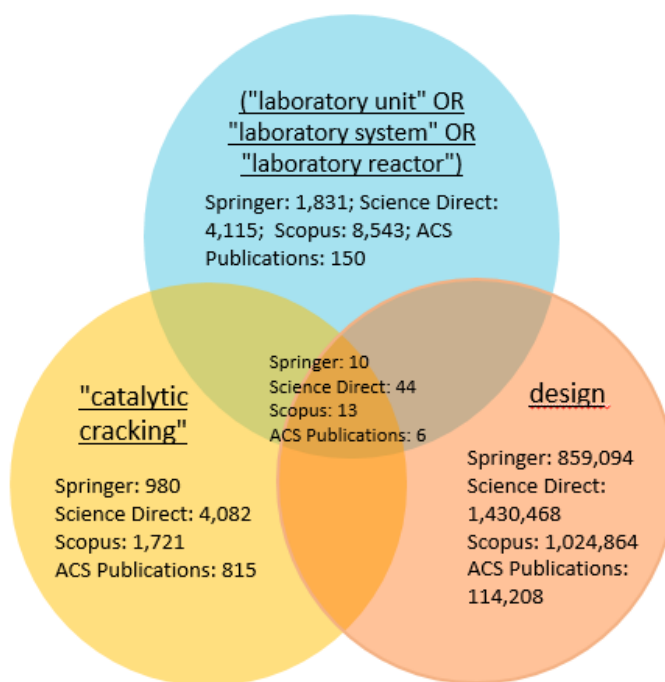


Figure 1: Venn Diagram for the search terms "*catalytic cracking*", ("*laboratory unit*" OR "*laboratory system*" OR "*laboratory reactor*") and design.

Table 1: Retrieved articles classification

	Cracking	Co-processing	Pyrolysis	Hydroprocessing
Fixed-bed	7 (24%)	6 (21%)	7 (24%)	9 (31%)
Fluidized-bed	17 (49%)	7 (20%)	11 (31%)	-
Combined units	8			

The catalytic processes (catalytic cracking and pyrolysis, co-processing and hydroprocessing) mentioned in the articles retrieved have a common purpose: to convert specific feedstock into fuels. In this review, studies concerning either laboratory scale catalytic cracking, catalytic pyrolysis, co-processing or hydroprocessing are organized according to the aforementioned criteria in the introduction section.

Generally, catalytic reactors are classified by the relative motion of the catalyst particles: fixed or mobile. Hence, in this review, laboratory size reactors are analyzed according to the motion of catalysts particles with respect to the fluid flow and the applied process. In heterogeneous catalytic processes, reactants are commonly in the gas or liquid phase and catalysts are solids in a fixed or a fluidized bed [3]. Examples of fixed-bed reactors are packed-bed [3], [40]-[41], trickle-bed [42], moving bed [7], [20], [43], structured (i.e., monolith and microchannel) [44], and stirred tank [45]. Other important example of fixed-bed reactors in the sense of catalytic process evaluations is the Micro Activity Test (MAT) Unit [33], [34], [46]-[49] and Short Contact Time-Micro Activity Test (SCT-MAT) [23], [41], [50]-[52]. MAT units are employed for the study of Fluid catalytic cracking (FCC) catalysts deactivation at laboratory scale [53]. Whereas, common mobile catalysts beds are: fluidized-bed, slurry reactors [44], Chemical Reactor Engineering Centre (CREC) Riser Simulator [18], [19], [21], [54], [55]., Advanced Catalyst Evaluation (ACETM) [29] and an Advanced Cracking Evaluation (ACE-RTM) [32]. ACE and ACE-R are similar to Micro Activity Test (MAT) Unit,

where the reaction cycle is made up of cracking, stripping, regeneration and purging steps. [29].

In general, when comparing briefly fixed and fluidized bed reactors, the former presents a simple design, reduced catalysts loss due to attrition and wear, and hence low investment and maintenance cost [3]. However, its disadvantages are that it usually operates in batch regime, it has poor contact of the fluid with the catalysts in situ, and presents poor heat and mass transfer rates as a consequence of the existence of gaps in the catalyst bed that behave as resistances, and hence is difficult to scale up [44]. While fluidized-bed reactors offer the advantages of high heat and mass transfer rates, resulting in a reaction rate limited process with a homogeneous product distribution [3], [7], [12]. In addition, the deposited coke on the catalysts surface can be gasified easily, resulting on the allowance of more continuous processes. These reactors are also capable of processing large amounts of feed and catalysts [3]. Nevertheless, fluidized-bed reactors require a high investment and operational costs due to the equipment required for the fluidization of the solid, the attrition and wear caused to the catalysts particles and the reactor walls, as well as the losses of catalysts due to carryover in the exit gas stream [7].

3.1. Laboratory fixed bed reactors for catalytic cracking

In the review, 7 articles studied the catalytic cracking reaction at laboratory fixed bed reactors. In general, all these units involve an oil injection system, a reactor oven, a pump connected to the evaporator, a reactor, a condenser, and a product receiver. The exit stream is connected to an analysis section in order to characterize the products obtained. For these researches fixed-bed reactors and Short Contact Time - Micro-Activity Test (SCT-MAT) units were employed to study its own and unique objective: the catalysts [23], [56]; optimization of specific feed and operating conditions of the process [41], [46], [47], [52]; and recent developments in catalytic cracking [15].

From the studies on catalytic cracking reactions with fixed bed reactors, just Zakarina et al. [52] mentioned the reactor volume; being in the range of 40-130 mL. In regard to catalysts to feedstock ratio, it was reported between 2-6 [41], [47], [56]. Just one author report the use of N₂ injection to the reactor [56]. Moreover, just two of articles indicate the use of Gas-Chromatography (GC) to analyze the gaseous products [23], [46].

The operating temperature of the laboratory reactor varied between 220-650 °C, at atmospheric pressure. The residence time of the reactants was set in a range of 0.5-60 s [15], [23], [47], and liquid feedstock flow rate was amidst 0.5 mL/min and 1.5 mL/h. This information is detailed in Table 2.

Feedstock applied in these studies were standard refinery products such as Heavy Vacuum Gas Oil (HVGO) or whole crude oils such as: Arabian Light (AL), Extra Light (AXL), and Super Light (ASL). Also different chemical reactants were studied to simulate bio-oxygenates or biomass-derived model compounds. Acetone, glycerol and n-hexane [41] [56] were employed for the former reason, while methanol, acetic acid, methyl acetate, 3-Methyl-2-penta-none, 2-Hidroxy-3-methyl-cyclopentenone, phenol, syringol, and trimethoxybenzene for the latter one [15].

Different catalysts were employed for the catalytic cracking studies in fixed bed reactors, such as: γ -Al₂O₃, Zeolite ZSM-5, and Equilibrium (E-cat) FCC catalysts. Some of them were impregnated with specific compounds [23], [52], [56] and others with MaximumOlefinsAdditive (MOA) [50].

A curious setup modification was carried out by Zakarina et al. [52], who employed an HP-PLOT/Q capillary column for the determination of the hydrocarbons products, CO₂, and H₂S. Whereas, Al-Absi et al. [46], [47] analyzed liquid products with a Shimadzu GC 2010-plus with FID, and the coke amount present on spent catalysts was evaluated with a carbon-sulfur analyzer from Horiba.

Table 2: Details of catalytic cracking experiments in fixed bed reactors.

Technology	Operating parameters	Feedstock	Catalysts employed	Target product
Fixed bed reactor [15]	T: 500°C; R.t.: 60 s	Methanol, acetic acid, methyl acetate, 3-Methyl-2-penta-none, 2-Hidroxy-3-methyl-cyclopentenone, phenol, syringol, and trimethoxy-benzene.	E-cat FCC catalysts	Gasoline
SCT-MAT laboratory unit [23]	T: 220–535 °C; P: 1 atm; R.t.: 0.5-1 s	HVGO	Zeolite modified with Ni and Co Nanoparticles	Hydrocarbon gases, CO ₂ and H ₂ S
SCT-MAT unit [41] [50].	T: 560°C	Acetone and glycerol, HVGO	ZSM-5 zeolite with MOA	Olefins and gasoline
MAT unit [46] [47].	T: 600-650 °C; R.t.: 30 s	Whole crude oils	E-Cat/ZSM-5 additive	C2-C4 light olefins, LPG, coke, and dry gas at the expense of naphtha, heavy cycle oil (HCO) and light cycle oil (LCO)
Fixed bed reactor [52]	T: 500-600 °C; Feed: 0.5-1.5 mL/h	VGO	HY zeolite catalysts on aluminum pillared natural calcium montmorrillonite	Gas, gasoline and light hydrocarbons
Displacement fixed-bed catalytic reactor [56]	T: 400-450 °C; P: 1 atm; Feed: 1.2 mL/min	n-hexane (liquid)	γ -Al ₂ O ₃ impregnated with Pt, Re, In and Ti	Methyl-substituted benzene, aromatic compounds and hydrocarbons up to C5

*T: Temperature; P: pressure; R.t. Residence time

3.2. Laboratory fixed bed reactors for catalytic pyrolysis

Fixed bed reactors employed for the evaluation of catalytic pyrolysis were found in 7 articles.

These reactors are the most common technology for slow pyrolysis due to the fact that this process involve low heating rates (5-50°C/min) and high residence time of solid and volatile compounds (>10s) [12]. In general, all of them counted with indirect heating method (external oven) and operated in batch regime. However, they worked with different feedstock such as microalgae [57], [58], waste tyre [12], and plastics [6], [27]. All of these reactors had a different analysis section for the products obtained.

From the catalytic pyrolysis reactions with fixed bed reactors, just Babich et al. [58] reported dimensions of the quartz unit they employed; 8 mm inside diameter, and 100 mm length. While Conesa et al. [43] mentioned the reactor catalyst bed height of 8 cm. Reactor fixed-bed was filled with 0.5 mg - 4.8 g of catalyst [27], [43], [57]. Reactors found for this section, employed different carrier gases such as argon [58], helium [27] and nitrogen [12], [57], [59]. Temperature for the catalytic pyrolysis in fixed bed reactors was set in a range of 300 - 600 °C [7], [12], [27], [58], [59], with the exception of [43], where a temperature of 900 °C for a metal recovering process through an oxidative pyrolysis was reported [43]. Residence time of the reactants went from 10 s to 60 min depending on the feedstock employed for the study; the shortest time for polyethylene [7], [27] and the longest belongs to microalgae pyrolysis [57]–[59]. Carrier gas flow rate varied between 15 – 500 mL/min from 10 min to 0.5 h. Waste tyre pyrolysis in fixed-bed reactors have been carried out with different feedstock capacity between 1 g – 3 kg [12]. The feedstock quantity used during waste plastics catalytic pyrolysis' in each run can vary from below 1 g to over 100 g [7], [27]. When the catalytic pyrolysis employed microalgae as the feedstock, researchers employed mass amount of around 3 g [57]–[59].

The catalysts employed for catalytic pyrolysis in fixed-bed reactors were mainly HZSM-5 and E-Cat. Furthermore, plastics catalytic pyrolysis in batch fixed-bed reactors provide higher gas product yields than in continuous regime [7]. The investigation retrieved with batch fixed-bed reactors, presented a gas and oil yield between 6.3 – 82.5% and 16 – 82.5%, respectively [7]., when the reactor was in continuous regime. The gaseous products obtained presented a yield in the range of 29.8 – 56.1%, and for oil was between 61.2 – 70% [7].

When evaluating tyre waste pyrolysis, operating pressure is not so important, but results of different authors have demonstrated that working under vacuum conditions has advantageous effects [12]. For waste plastics catalytic pyrolysis, the poor heat transfer rates

of fixed bed reactors obstruct higher feed amounts owing to the risk of producing large amount of melted plastic.

In reference to the products characterization, an interesting observation is that in the study by Aysu et al. [57], the gaseous products were not analyzed but the condensed liquid products were recovered by acetone washing. Lin et al. [27] connected the reactor online to a GC and also coupled to a mass selective detector (Agilent 5973) operating in electron impact mode (EI).

Details of catalytic pyrolysis in fixed-bed reactors are found in **¡Error! No se encuentra el origen de la referencia.**

Table 3: Details of pyrolysis experiments in fixed bed reactors.

Technology	Operating parameters	Feedstock	Catalysts	Target product
Batch fixed bed reactor [7]	T: 430-600 °C; H.r.: 5-25 °C/min.	LDPE, HDPE, PE, and PP	HUSY, HZSM-5, FCC, HZSM-11, Zn-HZSM-11, H β , MSM-41, Silica/Alumina, Pb-Co/BaTiO ₃ , DeLaZSM-5, and CaCO ₃	Gas and oil
Continuous fixed bed reactor [7]	T: 525 °C; Feed: 0.05 g/min.	PE	HZSM-5 and H-gallosilicate	Gas and oil
Fixed bed reactor [12]	T: 350-600 °C; P: vacuum, H.r.: 4-40 °C/min; Gas R.t.: 10-40 s	Waste tyre	CaC ₂ , MgO, CaCO ₃ , Al ₂ O ₃ , SiO ₃ , MgCl ₂ , γ -Al ₂ O ₃ , nano-HZSM-5 and many other catalysts	Gas, oil and char
CDS5200HP-R pyrolyzer [27]	T: 550 °C; H.r.: 20 °C/ms; R.t.: 15 s; He flow: 20 mL/min	WPE and WPP	Zeolite HZSM-5	Aromatic hydrocarbons
Moving tubular quartz reactor [43]	T: 900°C; Feed: 1mm/s; N flow rate: 500mL/min; R.t.: 40-80min.	FR4, CEM3 and ROGERS	Iron-clay catalysts	Gas and semivolatile species: polycyclic aromatic hydrocarbons

				(PAHs), bromophenols (BrPhs) and brominated dioxins and furans (PBDD/Fs).
Fixed bed reactor [57]	T: 400-600 °C; H.r.:100 °C/min; N ₂ Flow rate: 15 mL/min; R.t.: 60 min	Tetraselmis sp. and Isochrysis sp.	NiCe/Al ₂ O ₃ and NiCe/ZrO ₂	Bio-oil
Fixed bed reactor [58]	T: 300-450 °C, R.t.: 30 min, Ar flow: 100 mL/min	Chlorella vulgaris	Na ₂ CO ₃	Bio-oil

*T: Temperature; P: pressure; R.t. Residence time; H.r.: Heating rate

3.3. Laboratory fixed bed reactors for co-processing

From the articles retrieved, 6 of them described co-processing studies at laboratory fixed bed reactors [33], [34], [48], [49], [51], [60]. As presented in Table 4, most of co-processing studies found, have been carried out in a micro activity test unit (MAT) due to its utility of setting the time on stream time, catalysts/oil ratio, reaction temperature, regeneration times, gas flow, etc [29]. Moreover, the feed consisted of VGO as the petroleum component and with different biomass or pyrolysis bio-oils constituents. Authors evaluated different biomass sources in order to reach the highest yield for a biomass-based source of motor fuels and petrochemicals [33], [34], [48], [49], [51], [60].

Co-processing studies carried out in fixed bed reactors report just one reactor volume of 200 cm³ [60], others report specific dimensions such as internal diameter and length. The smallest reactor specified has 12 mm ID and length of 340 mm by Gueudré et al. [33], and the biggest has an internal diameter of 14 mm and length of 452 mm by the same authors years later [49]. A more detailed description of reactor dimensions are found in **¡Error! No se encuentra el origen de la referencia.** A catalysts mass between 2 – 11 g was packed in the fixed beds' reactors [33], [49], [60].

Before oil injection, most of the reactors were purged with Nitrogen. Also, the majority of MAT units reported for co-processing, were connected to an HPLC pump for feeding the

VGO and a separate syringe pump for the pyrolysis liquids. Liquid and gaseous products were collected in a receiver or a gas bag before being analyzed by GC.

When working with biomass, the reactor temperature was set in a range between 450-565 °C, but if the feedstock was composed of pyrolysis bio-oils, it ranged between 500-560 °C [29]. Reactor pressure was around 1.2 bar. Stripping under nitrogen lasted between 15 min – 1 h, with a flow in a range of 30 and 50 mL/min. Reactants residence time was between 30 s and 180 s. Catalyst/oil ratio varied between 1 – 8. All the studies employed equilibrium catalysts (E-CAT), some of them with a specific additive. The operating conditions are summarized in Table 4.

A novel reactor modification was performed by Gueudré et al.[49], who employed a MAT unit operating based on the ASTM D3907-03 (MAT unit from PID Eng & Tech) and modified for co-processing by addition of a second liquid injection pump. Gueudré et al. [33] used Argon as the carrier gas and for the stripping step. Also, for the regeneration step, they employed 20 vol.% of O₂ in Ar.

Table 4: Details of FCC co-processing experiments in fixed bed reactors

Technology	Operating parameters	Feedstock	Catalysts employed	Target product
MAT [33]	T: 500°C; P: 1.2 bar; Ar flow: 100 mL/min; R.t.: 1 min	HPO/CPO/VGO	E-CAT	Bio-fuels
MAT [34]	T: 482 °C; N ₂ flow: 30 NmL/min; R.t.: 180-360s	FPO/CPO/VGO	E-CAT	Bio-fuels
MAT [48]	T: 525 °C; N ₂ flow: 30 cm ³ /min	Rapeseed oil /VGO	E-Cat/ZSM-5 additive	Bio-fuels
MAT [49]	T: 560 °C; N ₂ flow: 50 mL/min; R.t.: 30s	Pyrolysis liquids/VGO	E-CAT	Second generation Bio-fuels

SR-SCT-MAT [51]	T: 520 °C; N ₂ flow: 40 mL/min	HPO/Atmospheric distillation residue	E-CAT	Bio-fuels
Fixed Bed microreactor [60]	T: 480-540 °C	Cotton seed oil, sunflower oil/ VGO	E-Cat, Halloysite nanotubes	Bio-fuels

*T: Temperature; P: pressure; R.t. Residence time

3.4. Laboratory Fixed bed reactors for hydroprocessing

Most of the retrieved articles that employed fixed-bed reactors mentioned hydroprocessing as their studied reaction. Hydroprocessing in fixed bed reactors was retrieved in 9 articles; including hydrogenation [61], hydrotreatment [62], [63], and hydrothermal liquefaction (HTL) [64]–[67]. This happens because the industrial process is always carried out at fixed-bed reactors. The hydrotreatment of petroleum distillates is performed at high hydrogen pressures, using large-volume three-phase reactors that present fixed catalysts beds, known as trickle-bed reactors.

Different kind of units appear with its own details for each process. For instance, a micro reactor, an HTL reactor, hydrotreatment units, and hydrocracking units. Most of them are models of existing industrial reactors [68], and others were constructed with specific modifications for the authors evaluation purpose.

Generally, a hydrotreatment laboratory reactor has a catalysts bed of 50 cm, a reactor diameter of 2 cm, and 0.15 L of catalyst. It is suggested that the unit presents a ratio of reactor diameter to catalysts diameter above 10, a ratio of catalysts bed length to catalyst diameter no less than 50, and a liquid flow rate of 0.012 cm/s [29], [68]–[70]. From the articles retrieved, the studies on hydroprocessing on fixed-bed reactors report different dimensions such as height from 30–70 cm, and volume capacities from 30 mL to 110 mL. Fixed beds volumes are in the range of 0.7 mL to 200 mL; the smallest belongs to a microreactor employed by Stavarek et al. [61], and the biggest from an isothermal fixed-bed up-flow reactor [71].

Reactors operating conditions varied at wide ranges of temperature and pressure depending on the process carried out between 80-525 °C and 1 to 300 bar. In regard to temperature, 2-methylpropene (isobutylene) hydrogenation carried out by Stavarek et al. [61], presented the lowest temperature range (80-120°C), while hydrocracking studies executed by Lopez et al. [7] were set at the highest temperature (475–525 °C). The lowest pressure interval belonged to the hydrotreatment units constructed by Aleksandrov et al. [68] (1-65 bar), and the highest was for an HTL reactor employed by Koley et al. [65] with 300 bar.

In general, the residence time of the reactants in all hydroprocessing studies was between 30-120 min. Feeding flow rate presented an extensive range from 1.5 to 247.7 NmL/min, reported for hydrogenation studies. Hydrogen/feedstock ratio was reported just for hydrotreatment units [68] with a value of 150-1500 m³/ m³. Stavarek et al. [61] also fed the reactor with nitrogen. Varieties of solid catalysts were employed for hydroprocessing, such as: Al₂O₃ with different metals (Pt, Pd, Ru, NiMo) [8], [61], [62], or HZSM-5 zeolites [66], [67]. But also homogeneous catalysts were used like CH₃COOH, H₂SO₄, KOH and NaOH [64], [65].

An interesting detail that Koley et al. [65] give is the heating rate of the reactor as 9-13 °C/min. Moreover, Z. Liu et al. [66] mention the stirring rate being of 380 rpm. An attractive fact detailed in one of the articles found, is the construction of two hydrotreatment units designed on the basis of tubular reactors. It is a two-reactor setup created for analogous evaluation of catalysts during hydrotreatment of diesel fuel and vacuum gas oil, as well as hydrocracking [68]. Additionally, Stavarek et al. [61] compared hydrogenation process in a microreactor and a conventional laboratory reactor, and could obtain higher hydrogenation rates in the microreactor. Even though, the rate was so intense that generated too much heat that influenced in the kinetics investigation and the dynamic behavior of the microreactor.

Table 5: Details of hydroprocessing experiments in fixed bed reactors.

Process	Technology	Operating parameters	Feedstock	Catalysts employed	Target product
Hydrogenation	Packed bed microreactor [61]	T: 80-120°C, P: 20bar, Feed: 1.5–247.7 NmL/min, continuous hydrogen flow; R.t.: 11-22h	Liquid 2-methylpropene (99.9%)	Commercial egg-shell catalysts with Pt/ γ -alumina	2-methylpropane
Hydrotreatment HDT	Continuous flow reactor system [62]	T: 400°C; P: 75 bar; R.t.: 1h	Bio-crude	C and gamma aluminium oxide supported, Pt, Pd, Ru and NiMo (5% load) catalysts	Upgraded bio-crude
HTL	Micro reactor [64]	T: 180-300 °C; R.t.: 30 min	Cyanidioschyzon merolae biomass	KOH, NaOH, CH ₃ COOH and H ₂ SO ₄ catalysts	Bio-crude
HTL	HTL reactor [65]	T: 200-300 °C; P: 100-300 bar; Holding time: 30-60 min; H.r.: 9-13 °C/min.	Wet Scenedesmus obliquus biomass	Homogeneous acid catalysts CH ₃ COOH, HCOOH, H ₂ SO ₄ , HCl, H ₃ BO ₃ , and the base catalysts NaOH, KOH, Na ₂ CO ₃ , K ₂ CO ₃ , Ca(OH) ₂	Bio-crude
HTL	HTL reactor [66]	T: 320-410 °C; P: 2.9 MPa; Stirring rate: 380rpm; R.t.: 60min	Nannochloropsis biomass	Fe/HZSM-5	Bio-crude
HTL	HTL reactor [67]	T: 380 °C; R.t.: 2h	Spirulina	Pd/HZSM-5@MS and Pd/HZSM-5 catalysts	Bio-crude

*T: Temperature; P: pressure; R.t. Residence time; **H.r. Heating rate**

3.5. Laboratory fluidized bed reactors for catalytic cracking

In this review, 17 articles studied catalytic cracking carried out in fluidized-bed reactors.

These reactors were reported for different types of studies such as: process control and automation [72], [73], CFD simulations [74], modeling [75], apart from experimental

evaluations [5], [7], [18], [19], [21], [54], [55], [76]–[78]. A specific type of fluidized bed reactor employed for various catalytic cracking studies is the CREC (Chemical Reactor Engineering Centre) Riser Simulator laboratory reactor [18], [19], [21], [54], [55].

According to the articles found, fluidized bed reactors employed for catalytic cracking had diverse reactor sizes such as diameters existing in the range of 0.075–38 cm, and height of 25–250 cm, with a bed of 4–20 cm height and ID of 5.3 cm bed, filled with catalysts in the range of catalyst/oil ratio from 1 to 8. All of the systems consisted of a pump connected to the evaporator, a reactor, a condenser, and a product receiver. Most of the feeding systems consisted of N₂ injector and a pump connected to the evaporator. One of the articles mentioned the mechanism employed to make RTD tests; being conductivity measurements by a micro-electrode [77].

Reactors operated at similar conditions to those in industrial FCC reactors; temperature was between 400–550 °C, with one article reporting a lower temperature range of 20–40 °C at a solid-liquid fluidized bed adsorber [77], and another study mentioned a higher temperature of 850 °C [75]. Pressure was set between 0.8–10 atm, with Qin et al. [55] mentioning that the reactor pressure is controlled via three transducers. Feedstock residence time was between 0.7–100 s, feed flow rate in a range from 0.2 mL/min to 1 L/h, and in some cases nitrogen flow of 200 mL/min as the carrier gas.

FCC Equilibrium catalyst (E-Cat) was the most common catalyst employed for catalytic cracking studies in fluidized bed reactors. Also, some authors reported the use of Y-zeolites, limestone, alumina-silica, silica sand, unsupported iron oxide/copper oxide impregnated on alumina and activated carbon as catalysts. Commonly, yields of 50–60% are reached in the process [79].

Suárez-Almeida et al. [75] reported the modeling of the transient response of a bubbling fluidized-bed biomass gasifier (FBG) which contained six thermocouples and two PID controllers, granting temperature control in the bottom bed and the freeboard, and also

recording four temperatures (one of the air preheating zone, two in the bottom bed, and one in the freeboard). The biomass feeding mechanism employed in this reactor consisted of a fuel hopper, a metering screw, and a fast rotating screw that inserts the fuel into a lower part of the fluidized bed [75]. In addition, these authors employed enriched air as a fluidization agent with the aim of keeping the gas velocity while the equivalence ratio (ER) was increased. Moreover, Khaled et al. [77] evaluated a fluidized bed reactor (FBR), which included a bypass with a valve that transported the excess water into the storage tank, and the water escaping from the upper part of the column was recirculating.

Table 6: Details of catalytic cracking in fluidized bed reactors

Technology	Operating parameters	Feedstock	Catalysts employed	Target product
Fluidized bed CREC-RSR [18]	T: 550 °C; R.t.: 5-30 s.	two feedstocks: a) a conventional FCC VGO, and b) a mixture of the VGO with 10%wt. of an atmospheric tower residue ATR.	FCC catalysts containing 30%wt. Y zeolite with different intracrystalline mesoporosity generated by alkaline desilication, on an inert silica matrix.	Mainly gasoline and LCO
CREC –RSR [19]	T: 450 °C; Feed: 0.2 mL/min. R.t.: 1-8 s	Decalin, a naphthenic bicyclic compound.	Commercial FCC catalysts in its fresh, equilibrium and three dealuminated forms.	Gasoline and LCO cuts
CREC- RSR[21]	T: 500 °C; R.t.: 0.7- 3.0 s.	FCC VGO feedstock (saturated SF, aromatic AF and resin RF)	two Y zeolites with different degree of mesoporosity	Gasoline
Bench-scale mini-fluidized batch unit CREC-RSR [54]	T: 550 °C; R.t.: 7 s	1,3,5-TIPB (1,3,5- tri-isopropyl benzene)	FCC catalysts	Oil
CREC-RSR [55]	T: 30 °C; P: 0–10 bar; R.t.: 3 s	benzene, N2, p- xylene, cumene, and n-octane, LDO- 70 and LDO-70S -- thiophene on the	0.15g Commercial FCC catalysts (LDO- 70 and LDO-70S) and REUSY zeolites (HRSY-1 and HRSY-3)	(FCC products)

		REUSY zeolites (HRSY-3)		
FCC risers [74]	P: 1.5-3 atm; air. Inlet velocity: 5.5 m/s; Gas + Solid inlet: 0.476 m/s.	Current FCC feedstock	A sand bed of 0.5 kg	(FCC products)
Laboratory scale bubbling fluidized-bed biomass gasifier (FBG) [75]	T: 850 °C; R.t.: gases (\approx 1– 10 s), biomass (\approx 10–100 s). Feed: 0.55–0.82 kg/h.	biomass (wood chips)	0.5 kg sand	syngas, and elutriated char
ACE confined fluid bed reactor (CFBR) [76]	T: 538 °C; P: 1.08 bar; Feed: 1.2 - 3 g/min; N ₂ : 140 cc/min; Catalysts R.t.: 30-120 s. Biomass R.t.: 1.5-6 s.	High sulfur (S = 2.39 wt%), non- hydrotreated, aromatic FCC feed and a light hydrotreated feed with a sulfur content of 0.23 wt%.	6-12g of equilibrium catalysts.	H ₂ , H ₂ S, C1, C2+, Gasoline, Coke, LCO, HCO
Circulating riser reactor (CRR) [76]	T: 538 °C; P: 0.8-1.4 bar, Catalysts flow: 100-500 g/min; Feed: 1.2 - 3 g/min; N ₂ : 140 cc/min.		4000g of equilibrium catalysts.	H ₂ , H ₂ S, C1, C2+, Gasoline, Coke, LCO, HCO
Solid-liquid fluidized bed adsorber [77]	T: 20–40 °C; Feed: 210–1000 L/h.	Water and NaCl as a tracer	activated carbon (industrial charcoal UP07)	Biofuels
Laboratory scale fluidized catalytic cracking (FCC) reactor [78]	T: 693 – 773 K. Feed: 10 mL/min. R.t.: 60 s; N ₂ flow: 200 mL/min.	pristine n-hexane and mixtures of representative compound of the bio-crude class, i.e. 1,2:3,5-di-O- isopropylidene- β - D-xylofuranose (DX) up to 50 wt% in n-hexane.	FCC catalysts	Green hydrocarbons

*T: Temperature; P: pressure; R.t. Residence time

3.6. Laboratory fluidized bed reactors for co-processing

From all the articles retrieved, 7 of them mentioned co-processing in fluidized bed reactors. Most of them simulated industrial FCC units containing a continuous catalysts regenerator. Moreover, there was found that these studies have been carried out in batch fluidized bed CREC Riser Simulator [18], [19], [21], [55], [80], ACETM [29] and an ACE-RTM [32].

With regard to the fluidized bed reactors employed for co-processing, just one author reported its cylindrical tube height being of 18 m [22]. In all the studies the catalyst/oil ratio was in the range between 3-8. The biomass component of these reactors' feedstock was diverse, such as: palm [29], pine [22] or canola oil [29], and the hydrocarbon component was VGO [18], [21], [32], [81], [82].

Temperature of these fluidized reactors was in the range of 500-550 °C, pressure from 1-2.4 bar, the feed flow was in a wide range of 1.2 g/min and 200 kg/h, residence time varied from 1-90 s to 2-3 h. Acidic commercial equilibrium FCC catalyst was the main catalyst employed for co-processing in fluidized bed reactors [18], [19], [22], [29], [55], [80]. Just one of the articles reported the use of USY+ZSM-5 [29].

Bezergianni et al. [29] mentioned a novel laboratory scale riser simulator reactor that contains an internal recycle reactor, where the catalyst is fluidized regularly in the course of the reaction. It also has an internal impeller for thrusting the feed and products gas throughout the catalyst bed. Moreover, the same authors describe a laboratory-scale two-stage riser fluid catalytic cracking unit that consisted of catalyst relay, staged reaction, optimum residence time and high catalysts to oil ratio. In the first stage riser, fresh feedstock is introduced and recycling oil goes into the second stage.

An implementation done by Ibarra et al. [82] to a reactor was linking the reactor to a vacuum box and a portion of product was transported to a chromatographic device. BASF Inc. and Kayser Technology employed an ACETM [29] and an ACE-RTM [32], respectively [29]. Most

of fluidized bed reactors were connected to an online standard capillary gas chromatography.

Table 7: FCC co-processing experiments in fluidized bed reactors.

Technology	Operating parameters	Feedstock	Catalysts employed	Target product
Fluid catalytic cracking (FCC) demonstration-scale unit [22]	T: 540 °C; P: 2.7 bar; Feed: 200 kg/h, R.t.: 2-3 h.	Raw bio-oil (co-product of pine woodchips fast pyrolysis commercial RTP unit). Standard Brazilian vacuum gasoil (VGO). Bio-oil/VGO weight ratios: 5/95 and 10/90.	Commercial FCC equilibrium catalysts.	Second generation fuel. Gasoline and diesel range products. Materials.
Laboratory-scale two-stage riser fluid catalytic cracking unit [29]	T: 500-520 °C	Palm oil/VGO	USY+ZSM-5	Bio-fuels
Advanced Catalysts Evaluation (ACE™) unit [29]	T: 490-530 °C	Canola oil/HAGO	9 g E-CAT	Bio-fuels
Advanced Catalysts Evaluation (ACE-R™) unit [32]	T: 530 °C, Feed: 1.2 g/min; R.t.: 90 s.	HPOFPO/HPO/VGO	E-CAT	Bio-fuels
Fluidized bed, batch CREC-RSR [80]	T: 500 °C; R.t.: 10 s.	Tetralin, phenol, syringol, and trimethoxybenzene; each mixed with tetralin (5 wt %) individually in benzene as an inert solvent.	0.3g an acidic commercial equilibrium FCC catalysts	Gases and C11+ hydrocarbons
RSR [81], [82]	T: 500-560 °C; R.t.: 3-10 s	FPO/VGO	E-CAT	Bio-fuels

*T: Temperature; P: pressure; R.t. Residence time

3.7. Laboratory fluidized bed reactors for catalytic pyrolysis

In the review, 11 articles study the catalytic pyrolysis reaction at laboratory fluidized bed reactors, including some hydrolysis processes. In general, these units include feed

reservoirs for biomass and catalysts, a gas distribution plate, a fluidized bed reactor, a collection vessel for char and liquid products, and the analysis section. These reactors offer fast heat transfer ($>100000^{\circ}\text{C}/\text{min}$), bed isothermicity that enhances pyrolysis oil yield, and either direct (using heating carrier) or indirect heating methods. The majority of reactors presented an external heating instrument. Most of the catalytic pyrolysis in fluidized bed reactors employ in situ mode catalysts, owing to the mixing regime of the solid, the isothermicity of the bed and the high gas-solid contact.

Some authors mentioned the dimensions of the units employed; having a general range between 30.5 cm and 20-30 m for the reactor height with an inner diameter going from 1 inch to 15.4 cm. Most of the feeding system consisted of an inert gas stream of N_2 and an evaporator unit.

Most of studies reported a reactor temperature between $350\text{-}511^{\circ}\text{C}$ in pressure range from 16-40 bar. The reported biomass residence time goes from 2-30 s and gas residence time was reported to be in the range of 1-5 s. Some studies were carried out in batch regime with a feedstock mass amount of 0.1-150 g. When operating in continuous regime, feedstock flow rate was between 1 g/min and 57.2 kg/h, catalysts velocity was around 10 m/s, and gas velocity in the reactors was of 7-15 cm/s. Additionally, some authors reported a nitrogen flow rate of 115 L/min [9].

Some studies presented non-conventional temperature ranges, for instance: a hydrolysis study operated at a low operating temperature of 30°C and high pressure of 105-180 bar in a slurry autoclave reactor [70]. On the other side, another study operated at a range between $500\text{-}1000^{\circ}\text{C}$ in an aerosol reaction system employed for the direct catalytic pyrolysis of hardwood bio-oil [1]. Also, a microwave-assisted pyrolysis study of lignin used a wide temperature range of $309\text{-}967^{\circ}\text{C}$ [83]. Microwave heating technology is an efficient bio-heating source for renewable fuels and chemicals that has already been applied in pyrolysis and solvolysis systems [83].

A wide variety of feedstock have been employed when talking about catalytic pyrolysis in fluidized bed reactors, including different types of plastics and biomass. The most common catalysts employed for the processes were: FCC E-Cat, $MgAl_2O_4$ and Al_2O_3 with different additives, and HZSM-5, HY and HUSY zeolites. Studies show that catalytic pyrolysis is a promising process; yields in continuous regime lie between 21-74 % and 15-91 % for gas and oil, respectively. And in batch regime, researchers obtained gas and oil with yields in the range of 6-88 % and 4-93 %, respectively [7], [12].

Chen et al. [1], employed superheated CO_2 steam to move individually oil and catalyst into the reaction zone. Also, they implemented a meticulous gaseous products detection and analysis section. The obtained products were carried out to a condenser and a particle fiber in order to remove remaining fine particles from the gas stream. In the gas detection section, the authors also employed a Nondispersive Infrared Sensor (NDIR) and a Gas Chromatography-Helium Ionization Detector (GC-HID). The gaseous products are collected and transferred to a molecular sieve/silica gel packed column for separation and analysis.

Another interesting reactor modification is the one carried out by Zhang et al.[84], who evaluated the use of a double fluidized-bed reactor system for a hydrolysis. In the first hydrolysis reactor, sand was employed as the fluidization media. The second fluidized bed reactor was employed to upgrade the vapors from biomass using a commercial hydrotreating catalyst. The reactor feeding system consisted of a high-pressure hopper-auger type feeder.

Table 8: Details of pyrolysis in fluidized bed reactors

Process	Technology	Operating parameters	Feedstock	Catalysts employed	Target product
	Continuous fluidized bed reactor [7]	T: 450-500 °C; Feed: 1 g/min - 9 kg/h	PE, PP-PE mixture, LDPE	FCC, $TiCl_4$, HZSM-5, HY,	Gas and oil

				and H β catalysts	
	Batch fluidized bed reactor [7]	T: 360-500 °C; Feed: 0.1-150 g	PE, HDPE, Polyolefin mixture + PS	HZSM-5, HY, HUSY, Mordenite, MCM-41, Silica-alumina, and FCC catalysts	Gas and oil
Catalytic Fast Pyrolysis in situ operation	Transported bed system with a riser reactor and a regenerator [20]	T: 500 °C; Gas flow: 15m/s; catalysts velocity: 10 m/s; Biomass R.t.: 2-3 s; Vapour R.t.: <2s.	Woody biomass	Pure ZSM-5 catalysts (diluted with a silica–alumina matrix).	CFP-oil, non-condensable gases, and char/coke
Catalytic Fast Pyrolysis in situ operation	Auger reactor [20]	T: 500 °C	Pine wood	ZSM-5 catalysts (diluted with a silica–alumina matrix)/sand mixture	CFP-oil, non-condensable gases, and char/coke
catalytic fast pyrolysis	Bubbling fluidized bed [4]	T: 501 °C; P: 1 atm. Throughput: 450 g/h; Feed: 156-222 g/h; N ₂ flow: 15 L/min; R.t.: 0.8 s.	Milled and sieved loblolly pine.	γ -Al ₂ O ₃ catalysts	Mostly biocrude rich in aromatic compounds, char and pyrolysis gases
	Modified version of the continuous Pyrolysis Process Development Unit (PPDU) [9]	T: 500 °C, Feed: 4.8-15.4 kg/h; N ₂ flow: 115 L/min.	Quercus rubra (red oak) wood chips dried to 10% or less moisture	1.6kg silica sand	bio-oil, char, and non-condensable gases
	Aerosol pyrolysis system [1]	T: 500-1000 °C; Feed: 0.8 L/min; R.t. 30 s	Hardwood oak-maple bio-oil	Commercial Ni powder catalysts, and activated	Renewable Hydrogen

				carbon powders.	
Fast catalytic hydrolysis	Slurry autoclave reactors [70]	T: 30°C; P: 105-180 bar	Spruce wood	Pd, red mud, NiMo, and CoMo catalysts	Bio-oil
Catalytic hydrolysis	Fluidized bed reactor [85]	T: 365-511 °C, P: 1.6-3.6 MPa.	beech wood	Mo/MgAl ₂ O ₄ , CoMo/MgAl ₂ O ₄ or NiMo/MgAl ₂ O ₄ catalysts	Bio-fuels
Catalytic hydrolysis	A double fluidized-bed reactor system (Zhang, Gong, Lai, & Alvey, 2017)	T: 425 °C; P: 21.7 bar; Feed: 1 g/min, gas velocity: 7-15 cm/s; R.t.: 2-6 s.	Red oak	Cogmmercial hydrotreating catalysts	Bio-fuel

*T: Temperature; P: pressure; R.t. Residence time

3.8. Combined units

From the articles retrieved for this review, 8 of them combine pyrolysis with in-line cracking reactions. The reactors configuration was diverse such as fixed bed/fixed bed, spouted bed/fixed bed, spouted bed/fluidized bed, fluidized bed/fluidized bed [86]–[88]. The former arrangement is the most commonly used. In addition, it was seen that when combining pyrolysis with catalytic cracking, the latter is commonly carried out in a fixed bed reactor, and the unit employed for the pyrolysis varies. In general, reactor dimensions consisted of 10 to 100 mm inner diameter and 910 mm height.

Two different arrangements have been presented for combined processes: a system composed of two fixed-bed reactors and a combination of a fixed and a fluidized-bed reactor. In the former combination, those apparatuses operated at a temperature range between 400-900 °C, the feed flow functioning in continuous regime was 0.06-2 kg/h and in batch regime it ranged between 0.04 g and 5 kg mass amount. The residence time varied between 4 s and 20 min [2], [89], [90]

Some authors [2], [86] worked with a fluidized bed reactor for the pyrolysis and a fixed bed reactor for the catalytic reforming of the volatiles produced, temperature was 450-500°C and 700°C for the fluidized and fixed bed reactors, respectively. Feed rate was 0.05-2 kg/h.

In addition, a system arrangement with two fluidized-bed reactors was presented by Barbarias et al.[87] and Erkiaga et al. [86]. For these cases, the operating temperature was 650°C for the first reactor (pyrolysis) and 850°C for the second fluidized bed (steam reforming), with 0.06 kg/h feed flow. Experiments were mainly carried out over HZSM-5 zeolite, but there were also reported other catalysts such as MXM-41 catalysts [7], HZSM-5 zeolite [7], alumina silicates [86], [87], sand/Ni-CaAl₂O₄ [7], [86]–[88], and pyrolysis carbonizates [2]. The gas and oil yield produced was 6.2-54.3% and 67.3%, respectively.

Ismail et al. [89] employed an electric-arc laboratory reactor for the production of hydrogen and nanocarbon through catalytic decomposition of electrocracking gases. This type of reactor is a stainless-steel vessel created for the pyrolysis of organic liquids in low-voltage electrical discharged. It consists of a vertical cylinder and a water jacket for loading the organic liquid waste. The reactor is equipped with permanent graphite electrodes in parallel. Finally, a Thermo-Catalytic Reforming (TCR) Unit was employed by Elmously et al. [2], which presented three divisions with different temperature zones, and heating rate of 200–300 °C/min.

Table 9: Details of pyrolysis in fluidized bed reactors

Technology	Operating parameters	Feedstock	Catalysts employed	Target product
Thermo-catalytic reforming (tcr) unit [2]	<u>Pyrolysis</u> : T: 400-500 °C; Flowrate: 2 kg/h feedstock input;	Sewage sludge	Catalytic reforming: pyrolysis carbonizates	Biofuels

	Residence time: 10 min, Heating rate: 200–300 °C/min. <u>Catalytic reforming:</u> T: 500-700 °C; R.t.: 4-5 s			
Conical spouted bed reactor and fixed bed reactor [86]	T spouted bed: 500 °C; T fixed bed: 700 °C	PE plastic feed	sand/Ni-CaAl ₂ O ₄ catalysts	Bio-fuels
Conical spouted bed reactor and fluidized bed reactor [86]–[88]	T spouted bed: 500 °C; T fixed bed: 700 °C	PE and PS plastic feed	sand/Ni-CaAl ₂ O ₄ catalysts	Bio-fuels
Electric-arc laboratory reactor [89]	T: 700 °C; P: 1 atm; R.t.: 20 min	700 mL of liquid organic waste (obtained from a local refinery)		Electrocracking gas
Electric-arc laboratory reactor connected to a laboratory flow setup which is an integrated fixed bed reactor [89]	T: 500-700 °C; P: 1 atm; Electrocracking gas flow rate: 6.976 or 13.330 cm ³ /min,	Electrocracking gas	GIAP-16 (NiO/Al ₂ O ₃) industrial catalysts	Highly pure Hydrogen, deposits of nanocarbon as by-product, acetylene, methane, and ethylene.
Fixed bed/fixed bed reactors [90]	T: 500°C and 800 °C for each reactor	PE, PP, PS, PET	-/Ni-Co-Al	Bio-fuels

*T: Temperature; P: pressure; R.t. Residence time

CONCLUSIONS

After discarding 48% of the articles for this Systematic Literature Review due to ineligibilities caused by not mentioning laboratory catalytic reactors, 28% from the 125 articles read mentioned studies that employed fluidized-bed reactors, being the 28% from the 125 articles read. 24% of articles used fixed-bed reactors for their experiments, and the other 6% employed combined units. Hydroprocessing studies resulted to be the most common reaction carried out in laboratory fixed-bed reactors, due to the fact that this process is always carried out in fixed-bed reactors at industrial scale. On the other hand, catalytic

cracking reactions are the most commonly reported studies in lab-scale fluidized-bed reactors.

With regard to the operating conditions; most of the reactors were set at a temperature of 400-550 °C and atmospheric pressures. E-Cat and HZSM-5 were the most common catalysts employed for the evaluations of catalytic cracking, pyrolysis, co-processing and hydroprocessing reactions. As catalytic pyrolysis is an attractive option to convert biomass-derived oxygenates into aromatic hydrocarbons, it shows a great percentage of studies in laboratory-fixed bed reactors and in combined units when carrying out the process with in-line reforming.

As mentioned before, researchers put great effort and interest on the catalytic cracking process. It is demonstrated with the total number of articles retrieved that studies concerning catalytic cracking processes sum up the highest number of articles considering fixed and fluidized bed reactors. Moreover, the great majority of described reactors, operate at similar conditions as industrial FCC reactors, as it is the most important process in petrochemical industries. Researchers investigate many aspects of FCC process such as: catalysts selection, feedstock, operating conditions, and the reactor setup. Different specific apparatuses for the laboratory evaluation of Fluid Catalytic Cracking aspects were reported; such as the Microactivity Test (MAT) Unit, the Advanced Catalysts Evaluation (ACETM) and the fluidized bed CREC (Chemical Reactor Engineering Centre) Riser Simulator Reactor (RSR).

In this SLR it was possible to compare and classify the design, application and operating parameters of the reactors mentioned in the articles retrieved. However, just 27% of the retrieved articles for this study mention their reactor dimensions and only approximately 50% of the papers describe the reactor components. This was a barrier to determine the best and most frequent reactor employed in terms of size and constituents. However, it could be seen that the future tendency on laboratory reactors, is the implementation of new technologies

rely on process intensification by improving mixing, heating and measurements devices, or applying novel product analysis techniques. As future work, it would be interesting to use this paper to design and build a novel and useful laboratory catalytic reactor for the studies that are carried out in some investigations.

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Annexes

Annex 1: MindMeister

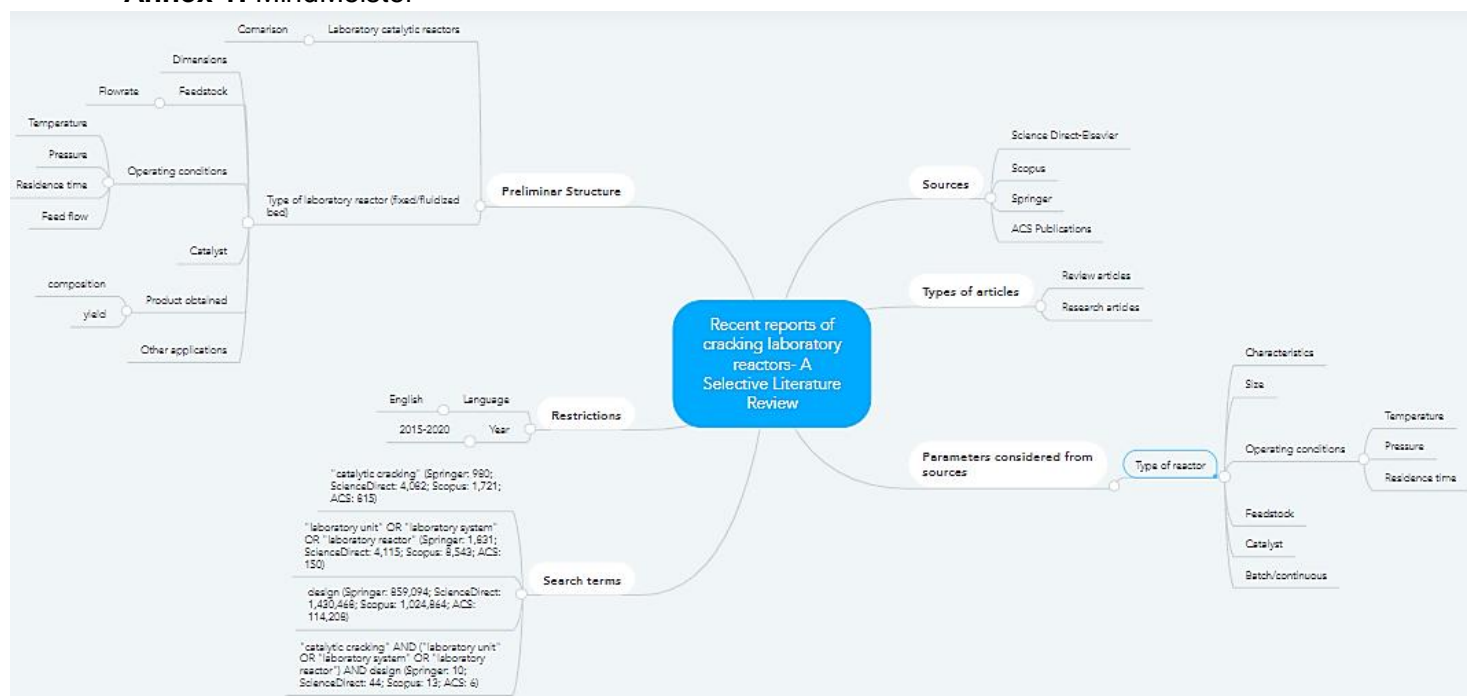


Figure A 1: MindMeister

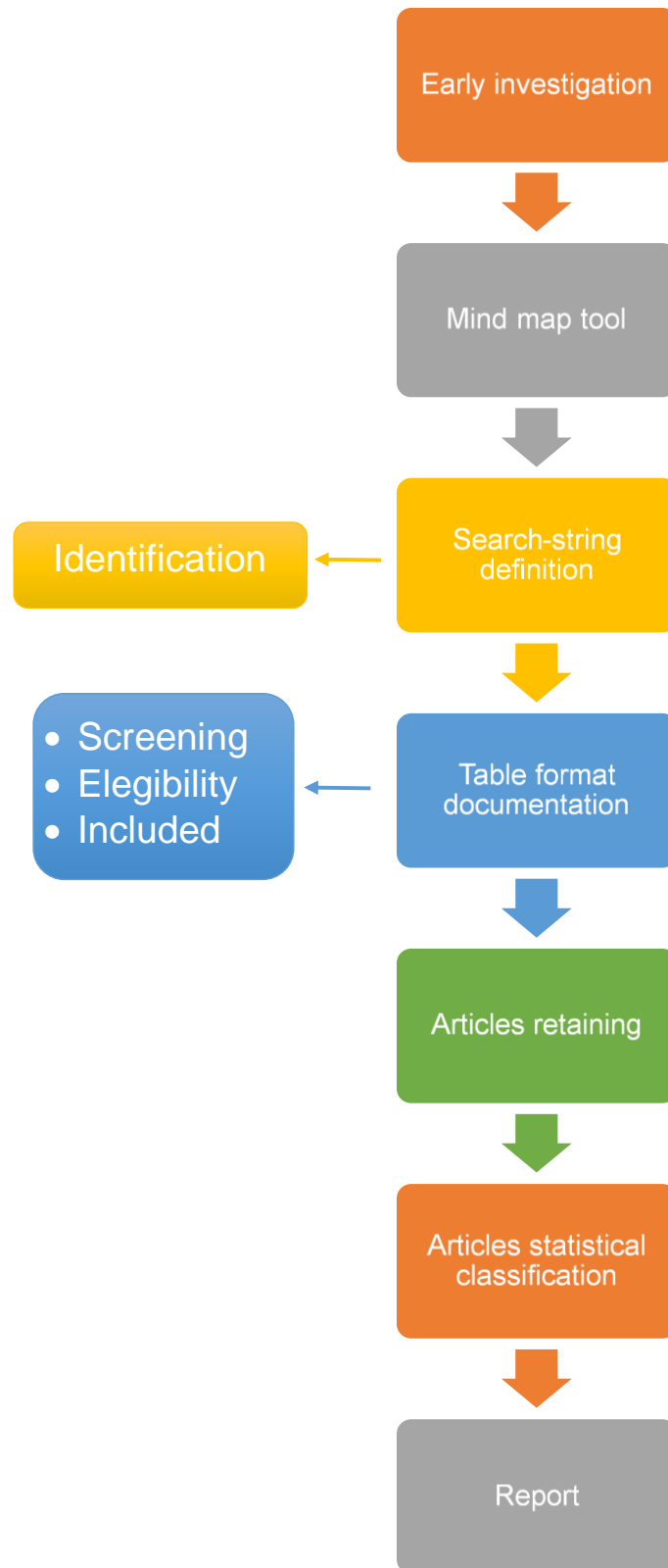
Annex 2: Methodology Block Diagram

Figure A 2: Methodology Block Diagram

Annex 3: Reactors dimensions

Table A 1: Reactors dimensions

FIXED-BED REACTOR		
Process	Reactor	Dimensions
Cracking	Short Contact Time - Micro-Activity Test (SCT-MAT) unit [41]	ASTM-MAT glass core catalyst bed: 1 cm diameter and 10 cm length. The reactor walls and glass core distance was 2.5 mm. The recovery system consisted of a 150 ml volume flask.
Cracking	SCT-MAT [52]	Different reactor volumes: 40-130 ml
Co-processing	MAT [49]	ID: 14 mm Length: 452
Co-processing	MAT [34]	ID: 14 mm Length: 318 mm
Pyrolysis	Fixed bed reactor [58]	ID: 8 mm Length: 100 mm
Pyrolysis	Fixed bed reactor [43]	Catalyst bed: 8 cm
Hydroprocessing	Packed bed microreactor [61]	Catalyst bed volume: 0.7 ml
Hydroprocessing	Hydrotreatment unit I [68]	OD: 16 mm Catalyst bed volume: 29 ml Height: 70 cm Catalyst bed thickness: 15 cm
Hydroprocessing	Hydrotreatment unit II [68]	OD: 22 mm Catalyst bed volume: 110 ml Height: 30 cm
FLUIDIZED-BED REACTOR		
Process	Reactor	Dimensions
Cracking	Bubbling fluidized-bed biomass gasifier (FBG) [75]	<u>Bottom bed:</u> ID: 53 mm Height: 200 mm <u>Bubbling fluidized bed:</u> ID: 81 mm Height: 257 mm <u>Transition zone</u> Height: 50 mm
Cracking	confined fluid bed reactor (CFBR) [76]	ID: 1.6 cm Bed height: 4.36-9.05 cm
Cracking	circulating riser reactor (CRR) [76]	ID: 7.5 mm Bed height: 995 cm
Cracking	circulating fluidized bed systems [5]	ID: 0.034-0.380 m Height of 0.71 - 2.5 m

Cracking	Plexi glass column of the fluidized bed adsorber [77]	ID: 9 cm Height: 140 cm Catalyst bed thickness: 8.5 cm
Pyrolysis	Laboratory bubbling fluidized bed [4]	<u>Reactor</u> ID: 6.3 cm Height: 25.4 cm <u>Disengagement section</u> ID: 10.2 cm Height: 101.6 cm
Pyrolysis	Transported bed system [20]	Riser length: 20-30 m
Pyrolysis	Bubbling fluidized bed [9]	<u>Plenum chamber</u> ID: 15.4 cm Height: 30.5 cm <u>Reactor</u> ID: 8.9 cm Height: 31.1 cm Catalyst bed height: 15.9 cm <u>Freeboard section</u> ID: 8.9 cm
Pyrolysis	aerosol reaction system [1]	Volume: 0.4 L
Hydropyrolysis	Double fluidized-bed reactor system [84]	ID: 1 inch
Thermal intermediate pyrolysis catalytic reforming	Thermo-Catalytic Reforming (TCR) Unit [2]	<u>Batch system</u> ID: 80 mm Length: 1000 mm <u>Catalytic reforming reactor</u> Height: 910 mm ID: 100 mm