

RESEARCH ARTICLE

Engineering

Review of the use of liquid fractions of bio-oils obtained from agricultural waste biomass

Revisión del uso de fracciones líquidas de bioaceites obtenidos a partir de biomasa de residuos agrícolas

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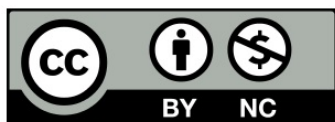
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The publication of this journal is funded by
Universidad ECCI, Bogotá-Colombia.

Editors: Robert Paul Salazar

Editorial assistant : Luz Adriana Suárez
Suárez.

How to cite: Alberth Gonzalez et al.,
Review of the use of liquid fractions of
bio-oils obtained from agricultural waste
biomass, TECCIENCIA, Vol. 17, No. 33,
1-12, 2022

DOI:<http://dx.doi.org/10.18180/tecciencia.2022.33.1>

Abstract. The transformation and use of agricultural and agro-industrial biomass has been the focus of study in recent years, due to its treatment and use in value-added products such as liquid, solid and gaseous fuels. Molecules such as hydrogen, organic carbon, organic nitrogen, oxygen, and oxygenated compounds present in the liquid phase of biomass currently represent opportunities for synthesis of green fuels and inputs for the industry. In this work was discussed the main aspects for Animal Biomass transformations from a perspective based on Biooils composition obtained from different thermochemical methods, containing model molecules, useful for biofuels synthesis for transportation.

Keywords: Agricultural Biomass, Oxygenated Compounds, Phenols, Lignocellulosic biomass, hydrodeoxygenation.

Resumen. La transformación y aprovechamiento de la biomasa agrícola y agroindustrial ha sido foco de estudio en los últimos años, debido a su tratamiento y aprovechamiento en productos de valor agregado como combustibles líquidos, sólidos y gaseosos. Moléculas como el hidrógeno, el carbono orgánico, el nitrógeno orgánico, el oxígeno y los compuestos oxigenados presentes en la fase líquida de la biomasa representan actualmente oportunidades para la síntesis de combustibles e insumos verdes para la industria. En este trabajo se discutieron los principales aspectos para las transformaciones de Biomasa Animal desde una perspectiva basada en la composición de Bioaceites obtenidos por diferentes métodos termoquímicos, que contienen moléculas modelo, útiles para la síntesis de biocombustibles para el transporte.

Palabras clave: Biomasa Agrícola, Compuestos Oxigenados, Fenoles, Biomasa Lignocelulósica, Hidrodesoxigenación.

1 | INTRODUCTION

On our planet, there are many biomass resources with a high energy efficiency, such as forest waste, agriculture, aquatic plants, municipal solid waste, animal waste, among others. These biomass sources represent potential chemicals and fuels. Fig. 1 shows the possible paths for using biomass of this nature and the typical equation design used for chemical equilibrium and reactor design from the main perspective using thermodynamic and kinetic parameters [1].

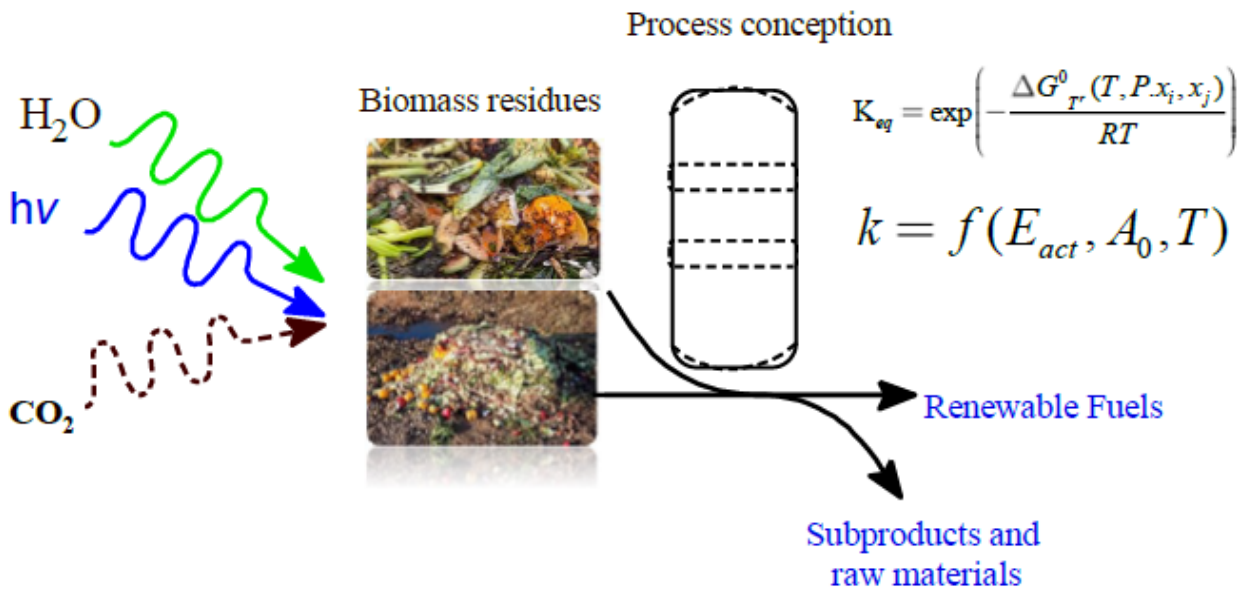


FIG. 1 . Friendly conversion of agricultural, animal, and agro-industrial biomass into fuels. Own source.

The continuous demand for food, in addition to the population growth in cities, has resulted in an increase in waste generation and atmospheric emissions. Especially, in agricultural and agro-industrial countries [2, 3]. Moreover, emissions from biomass of an agricultural, agro-industrial, and animal nature produce about 1.7 Mt CO_2 eq./yr (millions of tons of CO_2 equivalent per year) [4], thus generating a considerable impact on the carbon footprint and being potentially useful for the production of synthesis gas, energy, heat and chemical inputs [5].

Animal biomass is an interesting raw material for the development of energy harvesting processes due to the large amounts of produced methane and the liquid fractions of these residues containing nitrogen (N), phosphorus (P) and potassium (K). These are traditionally used as fertilizer and soil conditioner [6]. In recent years, the effectiveness of poultry manure as fertiliser has been questioned due to its low proportions of C/P and N, and to the high loss potential of N and P by leaching that contribute to increasing the environmental impact on wastewater [7]. These residues are usually recognised as a biomass fuel, with a physical appearance of similar consistency to a mixture of wood chips and sawdust. The moisture content of fresh waste can range from 20% to 50%. Its lower calorific power (LHV) usually varies between 9 to 13.5 MJ/kg [7]. Typically, when processing thermochemical biomass, three types of products are obtained [8]: liquid-phase bio-oils with high content of oxygenated compounds [9, 10, 11], [12] synthesis gas usually composed of hydrogen, carbon monoxide and traces of other elements such as methane, carbon dioxide, and some volatile compounds [13], and organic charcoal with concentrated oxidising organic carbon and acetyl compounds that give it a particular smell [14].

Animal biomass has been particularly processed for the development of agricultural inputs. As a result, it generates an environmental impact, due to the continuous production of gaseous emissions containing CH_4 , CO_2 and CO [15]. Additionally, the leachates generated in the processes for this type of biomass contami-

nate water sources [16]. For this reason, thermochemical or thermobiochemical treatments for fragmentation [17] represent an opportunity for the development of renewable chemical inputs with applications in the generation of bio-oils, in the agro-industrial sector [18], in the biofuels sector and in the processing of naturally sourced chemicals [19, 20]. Biomass usually has various chemical structures which must be accessible through prior treatments for defragmentation [21]. This allows the release of these molecules of an oxygenated nature [22] that contain fractions of hydrocarbons and precursor compounds for bio-refineries. Access to these molecules reduces energy costs of operation and processing by promoting processes at lower temperatures and pressures for transformation, as shown in Fig. 2.

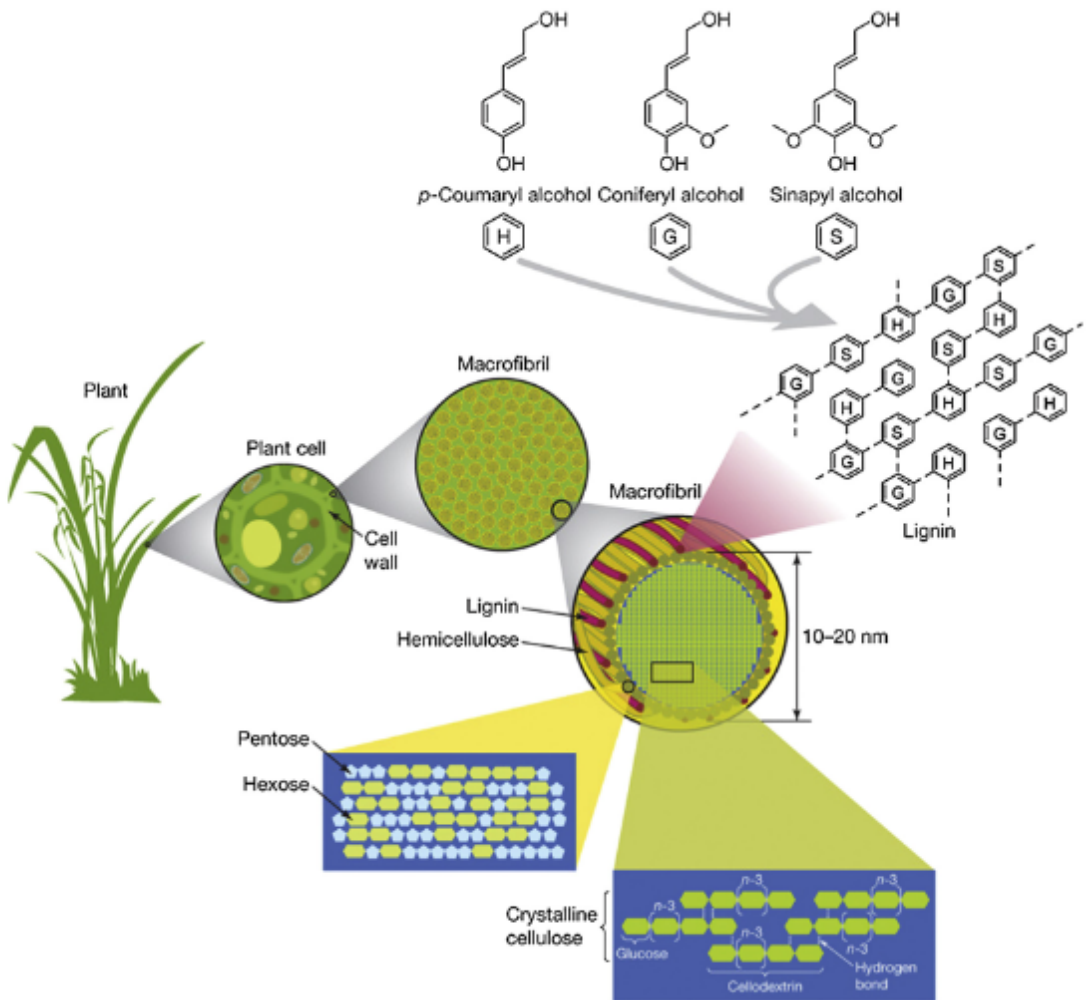


FIG. 2 Main fractions of Biomass, adapted from [9].

Physicochemical treatments include mechanical extrusion, drying and processes with alkali compounds that partially separate the organic structure from mineral and inorganic compounds, thus creating colloidal emulsions that facilitate their processing [7]. Regarding biological treatments, they are associated with the use of bacteria that defragment molecules according to the decomposition kinetics of the substrate or bacteria used. This is a slower process and generates by-products, such as light gases, when anaerobic conditions are used [8]. Bio-oils obtained from animal biomass contain important compounds in their structures, such as phenols, cyclic structures compatible with paraffin, acetate-type compounds that represent renewable matter for the production of plastics, and mild condensable gases. In the context of agriculture production, poultry waste represents a pollution problem, associated with the odours generated in this industry, and currently

there are no technologies to refine or process these wastes and give them a better final disposal. The main methods for using residual biomass are thermochemical processes, where biomass undergoes a heating process, with oxygen or in the absence of oxygen, which generate a spectrum of oxygenated compounds in the form of bio-oils, synthesis gas and solid organic fractions [9, 10, 11]. Fig. 3 shows the possible routes for using residual biomass and its conversion to its main products.

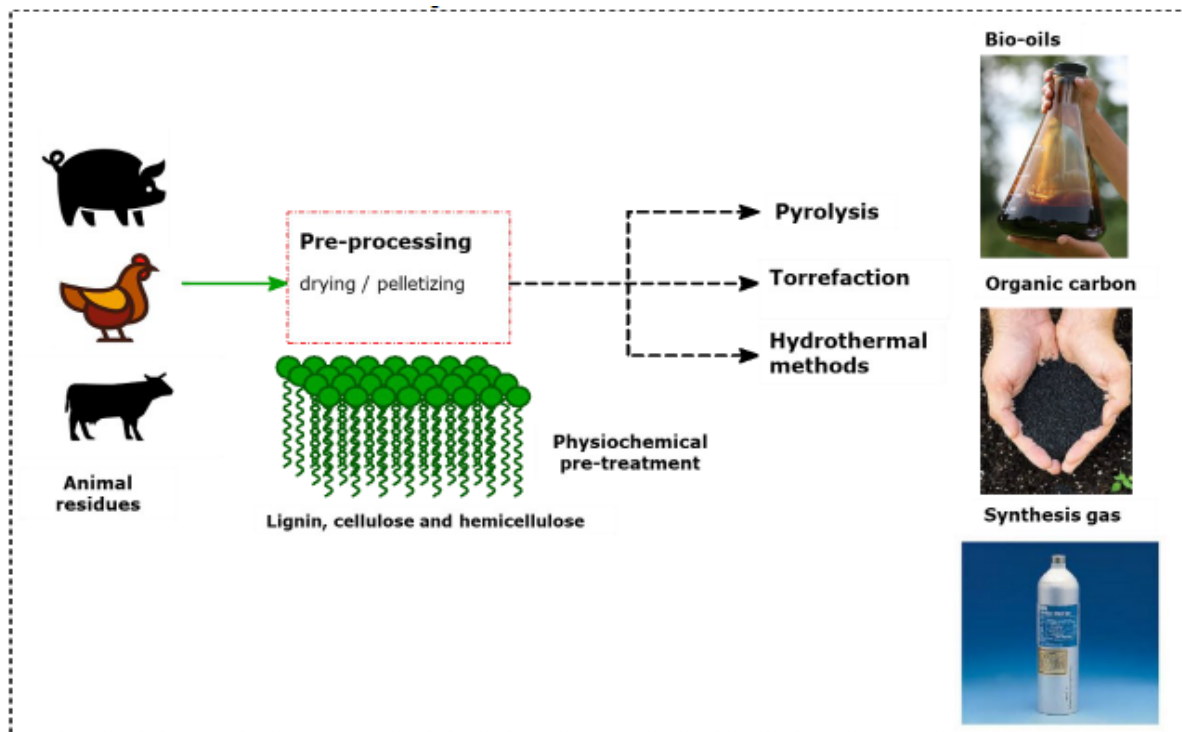


FIG. 3 Possible products and by-products obtained by thermochemical processes in the absence of oxygen for the production of renewable bio-oils. Own source.

The spectrum of molecules generated in these processes varies according to the process temperature, system pressure conditions, system flow configuration and catalyst use.

2 | CHARACTERISATION OF AGRO-INDUSTRIAL BIOMASS

Under the conception of a biorefinery, that is, considering the bio-oils generated in thermochemical processes as inputs for the production of biofuels, it is necessary to characterise the chemical composition of biomass and its main products, in terms of their potential for use. Biomass requires a pre- and post-treatment to be included as raw material in refining processes. These molecules can be inserted into catalytic cracking and reforming processes, similarly to oil, with modifications in operating conditions (P, T) and changes in the catalysts used in these processes [12]. Unlike petroleum, the composition of biomass is not homogeneous, as it is composed of animal waste, grains, wood, grass and biological residues, with elementary compositions of H, N, O and S, as shown in Table 1.

The average composition of bio-oils obtained by thermochemical processes in the absence of oxygen shows fractions of aromatic, oxygenated and long-chain compounds. This is interesting from the point of view of its use in catalytic processes for the production of biofuels and inputs. The processing technologies of this type of waste are in pilot phase, and some studies show a feasible picture for the production of biodiesel [23], biokerosene and biojet from phenol, furfural methyl molecules and animal fatty acids through routes of hydrogenation, hydrodeoxygenation and transesterification [17], and deoxygenation and transesterification

[18]. Additionally, the generation of synthesis gas at a smaller scale would theoretically allow the reuse of the hydrogen produced in the mentioned catalytic processes. Another possible route of use is the development of liquid phase reforming processes of these oil fractions, which would be potentially useful for the synthesis of paraffins and for bio-oil isomerisation processes [22, 23, 24]. Biomass needs to be depolymerised [25] and deoxygenated [26] in the vast majority of processes for biofuel production and value-added chemical compounds. Deoxygenation is required due to the high presence of oxygen molecules. It reduces the O_2 content and gives chemical stability and high polarity to biofuels formed from biocoaltes, thus facilitating their chemical compatibility with conventional fuels [27], such as gasoline, Jet A1 and conventional diesel[28].

TABLE 1 Thermochemical products expected in the different biomass conversion processes.

Raw material	Thermochemical Process	Conditions[P,T]	Productos
Chicken Poultry [29]	Fast Pyrolysis	[600-1000 °C]	C (35.59%)
			H_2 (4.57%)
			N (4.98%)
			S (1.45%)
			O (35.15%)
Pig Manure [30]	Licuefaction	[180-300 °C]	H_2
Sugarcane Baggase [31]	Gasification	[1050 °C]	CO_2 (13.69%)
			CO (13.69%)
			H_2O (10.70%)
			SO_2 (0.01%)
			C_6H_8 (0.15%)
			O_2 (4.21%)
			H_2 (13.91%)
			CH_4 (4.12%)
			N_2 (39.49%)
			H_2 (57,00 %)
Rice Husk [32]	Gasification	[1000 OK]	CO_2 (2,00 %)
			CO_2 (16,00 %)
			CH_4 (4,00 %)

3 | APPLICATIONS OF PRODUCTS OBTAINED FROM AGRO-INDUSTRIAL BIOMASS

The friendly conversion of residual biomass into bio-oils has potential for its use in biofuel synthesis. YAP et al. (2020) [33] developed a process of deoxygenation of chicken fat oil for the production of biodiesel on

bimetallic Ni-Cu catalysts supported on carbon nanotubes. The work evidenced that with the use of these catalysts, conversions greater than 70% are obtained for biodiesel, with physicochemical properties suitable for vehicular use. Moreover, within the production chain of this type of biomass, synthesis gas is a useful starting material for the synthesis of methanol and polymers on Cu catalysts [34]. Gonzalez A.R. reported the use of liquid and gaseous fractions of acetic acid and ethylene from the process of ethanol production from cane bagasse, for the synthesis of green vinyl acetate monomers using ethylene acetoxidation processes on nanostructured bimetallic catalysts of PdCu. The study showed that these renewable compounds can be used in the production of polymeric precursors [35]. Industrial production of biofuels from biomass is on the rise for two reasons: on one hand, governments aim to reduce atmospheric emissions from conventional fuels in the transport sector and, on the other, these foster the opening of new green markets that generate economic benefits, mainly for developing countries [36]. Currently, it is considered that the replacement of conventional fuels with biofuels should not exceed 5% [33], due to a negative impact on aviation engines.

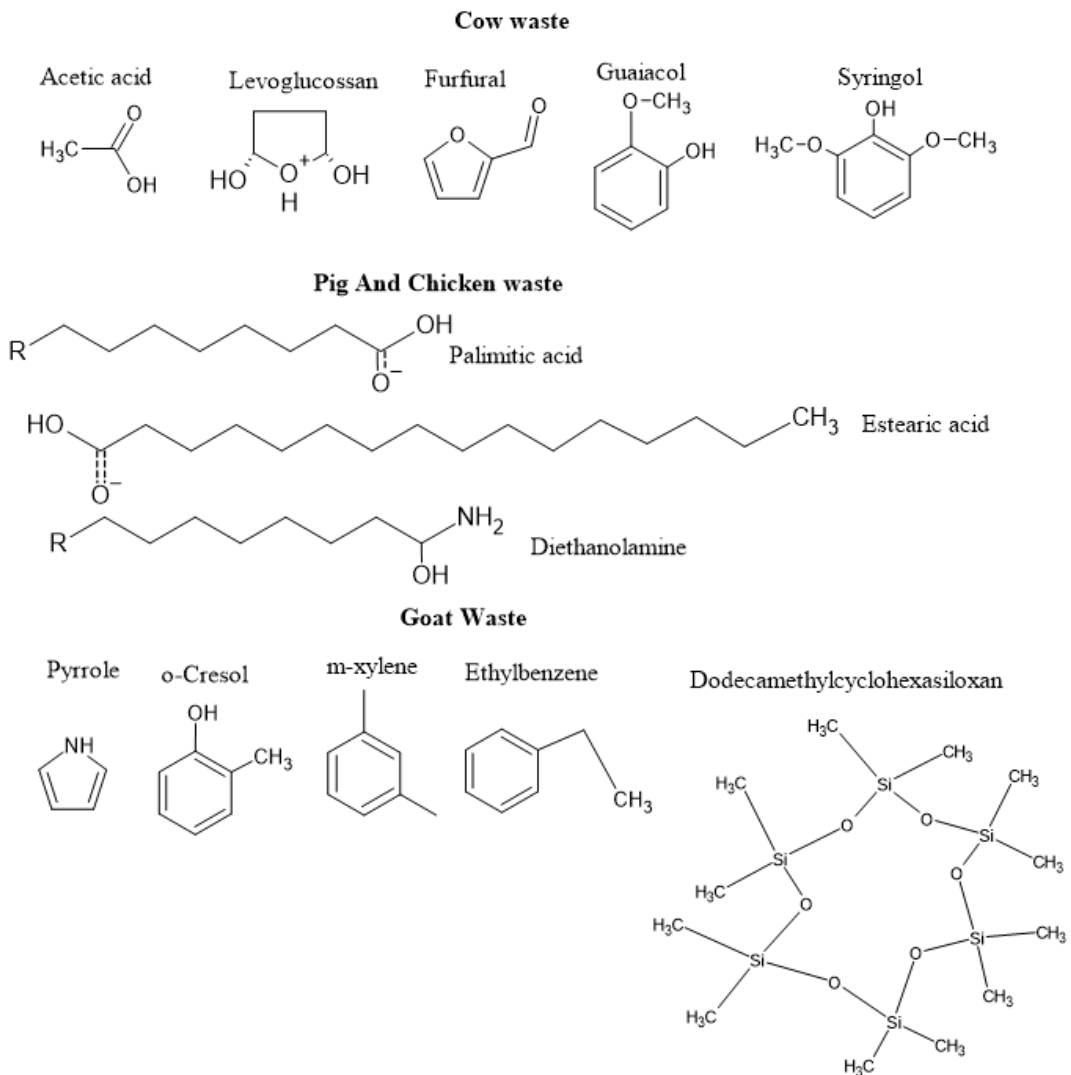


FIG. 4 Molecules present in bio-oils produced by thermochemical processes in animal biomass [13, 14, 15, 16].

In practice, this implies that the production chain of biofuels from biomass would only cover this degree of substitution, without relying exclusively on biodiesel and ethanol. A secondary line of these decomposition processes is based on the production and use of generated synthesis gas. This production process is affected

by the temperature and reactor type, as well as by the operational need to mix biomass with woody residues to improve calorific effects [37]. In addition to gasification processes in fluidized bed systems, catalysts are often used to promote the production of synthesis gas, thus improving hydrogen concentrations in the mixture by the effect of nickel catalysts as an active element in this type of heterogeneous reactions [38]. Several studies have shown the effect of process variables on gas production and its calorific power, for example, the effects of heating speed, flow rate and controlled temperature changes on fluidized beds [39]. Thermogravimetric studies represent the kinetics of biomass decomposition and how it is broken down into pyrolysis and gasification thermochemical processes. In the particular case of poultry waste, some TGA studies have shown decomposition at lower temperatures than typical residual biomass, reaching temperatures of 370 °C [40] with three stages of pyrolysis, due to its high hemicellulose and lignocellulose content, and three stages of devolatilization, with higher yields of synthesis gas and production of organic coal [41]. The decarbonization of carbonate minerals present in ashes of chicken manure showed an increase in CO₂ formation at temperatures above 700 °C, as a result of cracking at high temperatures [42]. Table 1 describes the main thermochemical processes for biomass conversion and the average composition of output gaseous products.

Bio-oil products from the thermochemical transformations listed in Table 2 allow the development of eco-friendly processes for catalytic conversion to value-added products, such as biodiesel [12] from poultry residues, biojet from fatty oils of pig residues [43] and production of green gasoline from goat residues through catalytic processes [44]. From this evidence, it is possible to visualise the future biorefineries that, in addition to processing and solving a constant problem of final disposal of waste, they may allow generating production chains of renewable compounds with different applications.

When catalysts are added to bio-oils, compounds produced resemble biofuels [45] with suitable properties for use in combustion engines. Typically, deoxygenation processes occur at high pressures and are assisted with catalysts to remove oxygen from their molecules, thus making them more similar to liquid fuels [46]. Juárez et al. (2020) reported the use of bio-oils from pig residues that, after undergoing a photobiocatalysis process [47], promotes the formation of organic bio-stimulants with high potential in agricultural applications. Baek et al [48] developed carbon catalysts with chicken manure bio-oils and took advantage of them in the process of heterogeneous phase transesterification of residual cooking oil for biodiesel production, obtaining conversions of 93%. Mayorga et al. [49] proposed strategies for the use of palm kernel in oil transesterification processes and found a possible reaction mechanism according to experimental evidence. In other processes for the production of biokerosene from these oil fractions, the catalytic process requires a hydrodeoxygenation stage and another stage of catalytic cracking, since aviation fuels must have a larger fraction of linear isoparaffins and paraffins [49], and smaller elements of phenolic and alkane compounds [50]. Currently, this process has the greatest advance in industrial scaling, being limited only by excessive oxygen consumption. For this reason, other technologies using zeolites under milder conditions allow obtaining a mixture of aromatic hydrocarbons with a lower degree of conversion in the catalytic process [51]. Ajak et al. [52] report a novel process of hydrodeoxygenation of bio-oil model molecules, including guaiacol and phenol on HY zeolites promoted with platinum, and found an excellent proportion of cyclohexane and alkylated cyclohexane with applications as conventional fuel. Additionally, catalytic hydrodeoxygenation processes have demonstrated excellent versatility in the processing of lipids from algae [52], as reported by several authors, with some limitations due to the leaching of algae fragments that do not react [53] and the catalyst poisoning, which depends essentially on the support metal interaction [54].

One of the challenges in the design of chemical systems for the production of bio-oils obtained by thermochemical processes is to find nanostructured catalysts that possess sufficient specific energy and adequate catalytic synergy to facilitate hydrogenation stages and the subsequent deoxygenation stage by releasing liquid fractions of biofuels [55], light gases and water. It is clear that a catalytic structure of this nature must have electronic properties associated with the generation of vacancies that allow the hydrogen to be transported and the oxygen of bio-oil to be removed by coupling without generating high losses of selectivity [56]. Several authors propose Ni-Mo catalytic systems [57], however, no studies have shown the effects of support-metal interaction so far, which allows the search for catalytic systems with electron dopants and donors that favour the process known as hydrogen spill over [58]. For this type of reaction, hydrogen spill over is an indicator

of materials that desorb water and release the formed products without affecting the stability of the catalytic structure.

4 | CONCLUSIONS

This review showed the fundamental aspects of the different processes of use of animal and agro-industrial biomass, which are the two most important lines in the circular economy. Taking into account the advances in biomass monitoring by energy organizations and unions, it is important to analyze the different processes of the use of molecules present in this type of biomass. This panorama can help to produce greater interest in the generation of green products and propose an effective solution to the problem of waste management in agro-industrial sectors. Poor management at the final disposal of these wastes generates a problem of polluting emissions and odors in neighboring communities. In terms of sustainability, these residues can be fully exploited due to the various fractions of aromatic compounds and fatty acids precursors of liquid biofuels. In regulatory terms, most tropical and developing countries have two authorized biofuel industries: the ethanol industry and the oil palm industry for biodiesel and bioethanol production. No other projects are being generated so far for biofuel production, but if the poultry industry continues to grow, this would lead to increased waste and polluting gas loads that could be framed by sustainable cleaner production policies focused on the production of biofuels for transport.

Acknowledgments

The authors are grateful to ECCI University, the GIATME research center and the mechanical engineering department.

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