catalysts

Editorial

Editorial Catalysts: Special Issue on Catalytic Pyrolysis

Gartzen Lopez [1,2]

[1] Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644, E48080 Bilbao, Spain; gartzen.lopez@ehu.es
[2] IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

Received: 28 April 2020; Accepted: 29 April 2020; Published: 30 April 2020

The increase of environmental concern is currently promoting the development of sustainable and green chemistry. In this scenario, a growing interest in biomass and waste valorization processes has been promoted in the last decades. Among these routes, thermochemical ones are those with the best perspectives for their full-scale development. Indeed, pyrolysis is an efficient and eco-friendly process for the production of fuels, chemicals, and hydrogen from different types of biomasses and wastes (e.g., plastics and waste tires) [1–3]. In addition, flash pyrolysis can be developed at full scale by using equipment that has reached a suitable stage in technological progress [4]. However, the commercial success of pyrolysis is restricted by the products' poor quality and the process's limited selectivity. Thus, biomass pyrolysis oil (or bio-oil)'s limited quality, especially its low heating value, poor stability, and corrosiveness, hinders its direct use as fuel [5–7]. In the same line, thermal pyrolysis of waste plastics gives way to wide product distributions, which limits the commercial perspectives of the process [3,8]. Therefore, catalytic pyrolysis is a feasible alternative to overcome the commented limitations of thermal pyrolysis. The incorporation of acid catalysts into pyrolysis processes has proven to be a key factor for the production of fuels and chemicals, such as light olefins and aromatics [6,9]. Furthermore, the use of reforming catalysts allows for the development of alternative routes for hydrogen production [10,11]. In spite of the interest in catalytic pyrolysis, there are challenges that must be addressed prior to its large-scale implementation, such as improving catalyst design, studies with real wastes, in-depth deactivation and regeneration studies, and the optimization of product distribution, to enhance the production of high value-added products.

This special issue includes relevant contributions in the valorization of different types of biomass by catalytic pyrolysis. Some papers in this especial issue present significant advances in the catalyst design field; moreover, interesting innovations in the development of catalytic processes are also reported. In addition, it also includes a complete review paper dealing with catalytic pyrolysis.

The paper by Bi et al. [12] pursues the development of highly selective and stable catalysts for biomass pyrolysis oil upgrading. Thus, hierarchical zeolites (HZSM-5 and Hβ) with an enhanced mesoporous structure were prepared by desilication, using an alkaline solution. The performance of these catalysts was evaluated in the catalytic cracking of Kraft lignin in a Py-GC/MS unit. Interestingly, a remarkable deoxygenation capacity, without higher coke deposition, was reported. The authors associated this improved cracking activity in relation to conventional zeolites with the reduction of mass-transfer limitations and the better accessibility of Brønsted sites.

Another paper published in this special issue incorporates the use of catalyst to biomass pyrolysis with a completely different purpose, i.e., to improve the hydrogen production. Solar et al. [13] proposed a novel strategy for the combined production of charcoal and hydrogen-rich gas in a two-step process. The first reaction consisted of a slow pyrolysis in a continuous auger reactor, aimed at charcoal yield maximization. In addition, a second catalytic reactor was included in the reaction unit for the in-line reforming of pyrolysis volatiles. Different catalysts with variable Ni loads were prepared; moreover, the influence of process conditions was deeply analyzed. It is notable that, by operating at high pyrolysis temperatures, high-quality char was obtained; in addition, the used suitable catalyst gave way to hydrogen concentrations of around 50% vol. in the gas product.

The performance of an original pyrolysis auger pilot plant in the valorization of sewage sludge was analyzed by Liu et al. [14]. The utilization of char as a catalyst was proposed for the upgrading of pyrolysis products, with a special focus on the increase in the gas product yield, because of its feasible application as fuel. The catalytic activity of pyrolysis char was analyzed, both using it in situ in the auger reactor and ex situ in a secondary fixed bed reactor. It is notable that the downstream catalysis showed a superior performance, with higher gas productions, in relation to in situ strategy. Moreover, the composition of the gas was greatly improved with the subsequent increase of its heating value.

The understanding of the catalytic role of biomass ashes in the thermal degradation process represents a significant challenge. Zhang et al. [15] analyzed the role played by biomass ashes under fast pyrolysis conditions in a py-GC/MS unit. Thus, biomass samples were impregnated with different amounts of H_2SO_4; the acid promoted the reaction between ashes and lignin to form lignosulfonates, which provoked the inhibition of their catalytic effect. Accordingly, the production of anhydrosugars can be enhanced as long as the degradation of these compounds to yield carboxylic acids, aldehydes, and ketones was suppressed. This study not only reveals the influence of ashes in biomass pyrolysis, but also proposes an interesting route for the production of valuable chemicals. In fact, a maximum yield of levoglucosan of 21.3% was reported under optimum conditions.

Moreover, the present special issue includes a review by Zhang et al. [16]. This paper widely analyzes the most recent advances in biomass catalytic pyrolysis and co-pyrolysis of biomass with plastic waste. Moreover, the application of different catalysts in this process was thoroughly revised. Other fundamental aspects of the catalytic pyrolysis process, such as the properties of the products, especially bio-oil and technological development, were also discussed in depth.

Acknowledgments: This work was carried out with financial support from the Spain's Ministry of Science, Innovation and Universities (RTI2018-098283-J-I00 (MINECO/FEDER, UE)) and the Basque Government (IT1218-19).

Conflicts of Interest: The author declare no conflict of interest.

References

1. Martinez, J.D.; Puy, N.; Murillo, R.; García, T.; Navarro, M.V.; Mastral, A.M. Waste tyre pyrolysis–A review. *Renew. Sustain. Energy Rev.* **2013**, *23*, 179–213. [CrossRef]
2. Kan, T.; Strezov, V.; Evans, T.J. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew. Sustain. Energy Rev.* **2016**, *57*, 1126–1140. [CrossRef]
3. Lopez, G.; Artetxe, M.; Amutio, M.; Bilbao, J.; Olazar, M. Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review. *Renew. Sustain. Energy Rev.* **2017**, *73*, 346–368. [CrossRef]
4. Chen, D.; Yin, L.; Wang, H.; He, P. Pyrolysis technologies for municipal solid waste: A review. *Waste Manag.* **2014**, *34*, 2466–2486. [CrossRef] [PubMed]
5. Bridgwater, T. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, *38*, 68–94. [CrossRef]
6. Valle, B.; Remiro, A.; García-Gómez, N.; Gayubo, A.G.; Bilbao, J. Recent research progress on bio-oil conversion into bio-fuels and raw chemicals: A review. *J. Chem. Technol. Biotechnol.* **2019**, *94*, 670–689. [CrossRef]
7. Mohan, D.; Pittman, C.U.; Steele, P.H. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy Fuels* **2006**, *20*, 848–889. [CrossRef]
8. Miandad, R.; Barakat, M.; Aburiazaiza, A.S.; Rehan, M.; Nizami, A.-S. Catalytic pyrolysis of plastic waste: A review. *Process. Saf. Environ. Prot.* **2016**, *102*, 822–838. [CrossRef]
9. Ayhan, D. Competitive liquid biofuels from biomass. *Appl. Energy* **2011**, *88*, 17–28.

10. Arregi, A.; Amutio, M.; Lopez, G.; Bilbao, J.; Olazar, M. Evaluation of thermochemical routes for hydrogen production from biomass: A review. *Energy Convers. Manag.* **2018**, *165*, 696–719. [CrossRef]
11. Tanksale, A.; Beltramini, J.N.; Lu, G. (Max) A review of catalytic hydrogen production processes from biomass. *Renew. Sustain. Energy Rev.* **2010**, *14*, 166–182. [CrossRef]
12. Bi, Y.; Lei, X.; Xu, G.; Chen, H.; Hu, J. Catalytic Fast Pyrolysis of Kraft Lignin over Hierarchical HZSM-5 and Hβ Zeolites. *Catalysts* **2018**, *8*, 82. [CrossRef]
13. Solar, J.; Caballero, B.M.; De Marco, I.; Lopez-Urionabarrenechea, A.; Gastelu, N. Optimization of Charcoal Production Process from Woody Biomass Waste: Effect of Ni-Containing Catalysts on Pyrolysis Vapors. *Catalysts* **2018**, *8*, 191. [CrossRef]
14. Liu, Z.; Singer, S.L.; Zitomer, D.; McNamara, P.J. Sub-Pilot-Scale Autocatalytic Pyrolysis of Wastewater Biosolids for Enhanced Energy Recovery. *Catalysts* **2018**, *8*, 524. [CrossRef]
15. Zhang, D.; Fan, Y.; Zheng, A.; Zhao, Z.; Wang, F.; Li, H. Maximizing Anhydrosugar Production from Fast Pyrolysis of Eucalyptus Using Sulfuric Acid as an Ash Catalyst Inhibitor. *Catalysts* **2018**, *8*, 609. [CrossRef]
16. Zhang, L.; Bao, Z.; Xia, S.; Lu, Q.; Walters, K.B. Catalytic Pyrolysis of Biomass and Polymer Wastes. *Catalysts* **2018**, *8*, 659. [CrossRef]