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# THERMOCATALYTIC PROCESSING OF PLASTIC WASTES AND BIOMASS INTO ADVANCED FUELS AND CHEMICALS

D. P. Serrano<sup>1,2</sup>

<sup>1</sup>Department of Chemical and Energy Technology, Rey Juan Carlos University, c/ Tulipán s/n, Móstoles, Madrid, Spain.

<sup>2</sup>IMDEA Energy, Avda. Ramón de la Sagra 3, Móstoles, Madrid, Spain.

e-mail: david.serrano@imdea.org

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## Abstract

The design and development of catalysts with properties tailored for the conversion of waste plastics into hydrocarbon mixtures, valuable as both advanced fuels and chemicals, has been the subject of a large number of research works in the past two decades. Processing plastic wastes by thermocatalytic routes faces a variety of technological and economic challenges that hinder its large-scale application. Plastics consist of very large macromolecules since strong steric and diffusional limitations are present when using conventional microporous catalysts. Novel generation of mesoporous catalytic materials (such as ordered mesoporous materials and hierarchical zeolites) have been successful in overpassing these limitations, although they suffer usually of a fast deactivation due to both coke formation and poisoning by the impurities present in the raw plastics. Accordingly, plastic wastes conversion by direct contact with the catalyst, although having an evident scientific interest as a very sensitive test reaction, it is difficult to be implemented at commercial scale. In this way, many of the process proposed for the thermocatalytic conversion of plastic wastes involve the combination of two steps: thermal conversion of the raw residues followed by the catalytic reforming of the so produced liquid oil. The latter can be accomplished in an inert atmosphere or in the presence of hydrogen in order to reduce the olefin concentration and to remove heteroatoms, as well as to decrease the catalyst deactivation by coking. Thereby, in addition to a high accessibility, the catalysts must share a right balance of acidic and hydrogenating functions, which requires the incorporation of metal phases onto acidic supports. However, the cost of hydrogen, the metal price and the use of moderate pressures are factors to be considered as they may affect negatively the process economy.

On the other hand, a high interest has arisen in recent years in novel processes for the transformation of different types of biomass into advanced biofuels. The use of non-edible biomass sources and the overall sustainability of the process are very important factors to be considered in the development of new routes for the production of second-generation biofuels. In this way, lignocellulosic biomass appears as a very interesting source of biomass due to its independency with the food market, its low cost and high availability in the form of agriculture and forest residues or as energy crops. Three main pathways are being explored for the thermochemical conversion of lignocellulose: gasification, pyrolysis and liquefaction. Biomass pyrolysis, depending on the temperature and the heating rate, yields gases, liquid and solid fractions with different proportions. The maximum yield in the liquid fraction (bio-oil) is attained when working at temperatures of about 500°C and high heating rates (fast and flash pyrolysis). This is a relatively simple process that it is being implemented now at commercial scale in different countries. However, one of the unsolved problems is related to the complex composition of the bio-oil, which limits its use as fuel mainly in not very demanding applications, such as heating fuel. Bio-oil presents both high oxygen content and low calorific value. Moreover, it has an acidic pH, which provides it with undesirable properties. Accordingly, a variety of routes are being investigated for bio-oil upgrading into advanced biofuels, showing properties suitable for the transportation sector. These routes include a number of chemical transformations, such as catalytic pyrolysis, hydrodeoxygenation, ketonization, esterification, aldol condensation, alkylation, etc. In most cases, the catalysts to be developed should combine bifunctional properties, for removing a large part of the oxygen contained in the bio-oil and to modify the chemical structure of the compounds for its use as transportation fuels, with a high accessibility to the active sites.

The similarities existing between several of the thermocatalytic routes for the conversion of waste plastics and biomass is evident, so much of the experience gained in each field can be of interest in the other one. Moreover, this similarity opens also the way to the development of processes that could transform simultaneously both type of raw materials into advanced fuels and chemicals.

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