



Catalytic Dry Reforming for Biomass-Based Fuels Processing: Progress and Future Perspectives

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Dedication to Professors George A. Olah and G. K. Surya Prakash for their contribution in carbon dioxide valorization

We describe and review recent research on potential biomass-derived fuels consisting of methanol, ethanol, butanol, and carboxylic acids. These fuels possess a volumetric energy densities of 15.6–22.7, 20.9–26.8, and 24.6 (levulinic acid) MJ L⁻¹, respectively. We recognize biomass as a valuable, sustainable, and economic fuel source in comparison to fossil fuels. First, we discuss, characterize, and compare all men-

tioned fuels. Second, we review recent research developments in the continuous pre-processing for syngas production for biofuels production, specifically concentrating on dry reforming and the catalytic effects on the effluent and process efficiency. Finally, we discuss the future prospects and research needs to realize this technology on a global scale.

1. Introduction

The growing concerns related to petroleum-based fuels together with the environmental and health regulation have brought forth the necessity to develop clean technology approaches for energy production using new-generation of fuels.^[1–6] Catalytic reforming of hydrocarbons (HCs) with CO₂ seems to be a promising technology to produce syngas, which can be applied as a fuel, that is, for fuel cells or for the synthesis of valuable oxygenated chemicals.^[7–12] Synthesis gas is conventionally produced via HC steam reforming; however, increased concerns on the contribution of greenhouse gases to global warming have focused interest in the replacement of steam as reactant with carbon dioxide to help in wastes conversion in the valuable product chain.^[13,14] Catalytic conversion of light alkanes by reforming with CO₂ (dry reforming, DR) enables the use of HCs in the generation of synthesis gas with a low H₂/CO ratio and thereby reduces the CO₂ and HC emissions. It has been observed in the open literature that syngas is a very good option to substitute fuels for internal combustion (IC) engines, showing acceptable engine performance.^[15]

The DR investigations are mainly focused on fuels such as natural gas and methane, whereas the DR of lignocellulose-based fuels such as ethanol (EtOH), methanol (MeOH), and carboxylic acids (RCOOH), are less studied.^[12,13,16,17] Almost 90% of the research contributions during the last five years are devoted to develop active, highly durable, and stable catalysts suitable for application in DR for continuous gas supply and using a suitable CO/H₂ ratio for downstream industrial processes. Ethanol and biodiesel are the two main biofuel products.^[18–23] The most widely used biofuels are ethanol mixed with gasoline and biodiesel mixed with diesel petroleum fuel. Hence, there are different biofuel levels in the mixtures depending on the level of bio-derivative in the

blends. The blend level, similarly for biofuels, is indicated by the first letter of the greener fuel, that is, E followed by the percentage level of mixture (e.g., E10 in EtOH case indicates a 10% level of bio-ethanol and 90% of gasoline as a very common blend). The pure ethanol fuel E100 can be found in Brazil, which is recognized as one of the highest EtOH producers.

Sustainable energy sources and biofuels can help to reduce greenhouse gas emissions, presenting at the same time high energy efficiency, that is, the energy produced by the biofuel minus the energy consumed during the production process (Figure 1). On the other hand, there are some concerns related to biofuels such as economic efficiency and unknown negative environmental aspects, which are still today very difficult to predict.

Investigations are directed towards the second-generation of biofuels to eliminate any negative consequences in competing with food production and to enhance the production efficiency by using a much greater range of plants and plant waste.^[18–26] The catalytic transformation of platform mole-

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