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 mentioned 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.[18–25] 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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cules into liquid hydrocarbon fuels appears as an interesting approach for the production of advanced biofuels and for the gradual replacement of used fossil fuels and fuel additives.

The objective of the present review is to evaluate and integrate recent basic research on potential biomass-derived fuels consisting of methanol, ethanol, and carboxylic acids and their catalytic dry reforming for syngas production. A brief evaluation of the above-mentioned fuels is also provided. Moreover the main research achievements attained thus far are reported, including the catalyst application in fuel processing technologies. Finally, the remaining research challenges as well as future prospects are described.

### 2. Biomass-Based Biofuels

Next-generation biofuels, such as cellulosic bio-ethanol, C$_1$–C$_2$ organic acids from waste, synthetic biofuels obtained via gasification of biomass, bio-hydrogen, and others, are currently at the center of the attention of technologists and policy makers in search of the more-sustainable biofuel of tomorrow.[18–23] The biomass-derived fuel examples are presented in Figure 2, and the properties of the selected biofuels are summarized in Table 1 and compared with gasoline.

![Figure 1. Carbon-neutral bioenergy](image)

![Figure 2. Biomass-derived biofuels: a) bio-syngas, b) bio-methanol, c) bio-ethanol, d) bio-butanol, e) levulinic acid, f) gamma-valerolactone, g) 2-methyltetrahydrofuran, h) delta-amino levulinic acid, i) levulinic acid esters.](image)
Additionally, the lignocellulose-based feedstock can be converted into gaseous, liquid, or solid fuels, for example, syngas, bio-ethanol, or other valuable products. Importantly, they are accepted as an alternative fuels of growing interest (Table 2).

### Table 2. Gaseous and liquid biofuels derived from cellulose biomass.

| Fuel  | Process      | Catalyst                      | Ref. |
|-------|--------------|-------------------------------|------|
| methan e | DR          | Si/CeZrO<sub>2</sub> | [33] |
| methanol | DR          | Al<sub>2</sub>O<sub>3</sub>/CeZrO<sub>2</sub> | [34] |
| bio-ethanol | SR, DR  | Group VIII supported on | Al<sub>2</sub>O<sub>3</sub> | [37] |
| ethanol  | SR + chemical looping | Ni<sub>2</sub>Al<sub>2</sub>O<sub>4</sub> | [38] |
| methanol, ethanol | fuel cells | Ni/SiO<sub>2</sub> | [39] |
| biomass | gasification, SR, DR | Ni/olivine | [41–44] |
| toluene | SR          | Ni/olivine | [39] |
|         |              | LaNi<sub>5</sub>F<sub>3</sub>,Ce<sub>2</sub>O<sub>3</sub> | [40] |

2.1. Bio-syngas

The syngas obtained from lignocellulose-based feedstocks can be directly used to power internal combustion engines (ICEs) as presented in Figure 3, eliminating the emission problem of noxious pollutants such as nitrogen oxides (NO<sub>x</sub>), sulphur oxides (SO<sub>x</sub>), and particulate matter (PM), particularly in crowded urban areas. The high power density, ease of transportation and storage, and many years of development of IC engine technologies have put liquid petroleum-based fuels (PBFs) at a privileged position in our energy sector. The growing concerns related to PBFs together with environmental and health regulations indicate the necessity of rational and clean technologies for both energy consumption and energy production, ideally based on renewable sources and even wastes. Moreover, the quality of life and prosperity of the people in urban areas rely upon efficient and sustainable energy production, and the economic and individual development of citizens depends also on affordable and adaptable transport and energy generation/consumption options.

To overcome the negative effects of fossil fuels, in 2007 the European Union (EU) agreed to the 20–20–20 objectives: a 20% reduction in greenhouse gas (GHG) emissions compared with 1990 levels, a 20% renewable energy market share, and a 20% improvement in energy efficiency.

Paris also recently hosted the 21st Conference of the Parties to the United Nations Framework Convention on Climate Change (COP21/CMP11), addressing the topic of reducing CO<sub>2</sub> emissions. A historic agreement to combat climate change and to keep global warming below 2 K towards a low-carbon, resilient, and sustainable future was agreed upon by 195 nations during this conference. In this context, the utilization of cheap, abundant, safe, and renewable sources of energy for the production of fuels and chemicals is essential. This applies particularly to biomass; the best scenario is with lignocellulose biomass, which contains three major components: cellulose (∼35–50%), hemicellulose (∼20–35%), and lignin (∼10–25%), as a potential alternative feedstock to fossil fuels due to its high abundance, biodegradability, and remarkable sustainability as well as the low amounts of toxic gases (such as sulfur oxides and carbon dioxide) that are released during processing.

2.2. Bio-methanol

Bio-methanol is the simplest and cheapest among the alcohols with the formulation CH<sub>3</sub>OH. It is a clear liquid with density (792 kg m<sup>–3</sup>) lower than that of water (1000 kg m<sup>–3</sup>) and blends well with gasoline (745–803 kg m<sup>–3</sup>) or diesel oil (833–837 kg m<sup>–3</sup>) to be used as fuels in internal combustion engines or electricity generators. Already blends M10 and M85 are available for use in thousands of vehicles, and methanol blends have also been investigated for use as fuels for shipping. Using bio-methanol a wide range of chemicals can be produced, including bio-methyl tertiary butyl ether (MTBE) to increase the octave level in petrol by preventing the “knocking” effect. Bio-methanol can be produced from a wide range of biomass feedstocks by using a thermochemical route similar to the Fisher–Tropsch (FT) process from biomass to liquid (BtL) currently, most methanol is produced by the catalytic conversion of syngas from fossil sources. Methanol and/or dimethyl ether (DME) can also be produced by an economical method, as shown in Figure 4, by using carbon dioxide and any methane source or natural gas in the specific process known as BI-REFORM-
This process consists of a combination of steam and dry reforming, in a specific ratio to produce a 2:1 molar ratio of hydrogen and carbon monoxide with subsequent conversion of the CO and H\textsubscript{2} mixture exclusively to CH\textsubscript{3}OH and/or DME.[28,31]

Within the EU Biofuels Technology Platform[32] several bio-methanol-related projects on different stages can be found including (i) demonstration projects and commercial production of bio-methanol using glycerin as a feedstock, (ii) innovative process development for the production of bio-methanol using various feedstocks, including crude glycerine, biomass, and CO\textsubscript{2}, (iii) syngas-to-methanol process development and a methanol-to-ethanol conversion unit, (iv) methanol and solid-oxide fuel cell (SOFC) technology for shipping as well as the development of gasoline/ethanol/methanol blends (GEM Fuels) for use in racing cars.[47]

### 2.3. Bio-ethanol

Bio-ethanol is a clear liquid at room temperature, which has lower density than water and mixes readily with water and gasoline. The energy content falls in the range of 20.9–26.8 MJ L\textsuperscript{−1}. First-generation bio-ethanol is usually made from agricultural crops. In Europe, wheat is the main crop grown for bio-ethanol production. The production process consists of three subsequent steps: (i) hydrolysis (conversion of carbohydrates into monosaccharides by an enzymatic route or using acids in a hybrid biochemical–chemical process), (ii) fermentation (enzymatic conversion of monosaccharides into ethanol), (iii) distillation (separation ethanol from the feedstock). A second-generation bio-ethanol, cellulosic ethanol, can be produced from a wider range of feedstocks, including agricultural residues, woody raw materials, or energy crops that do not compete directly with food crops for land use.[18–23,27,28] For the future, the biodegradable fraction of municipal solid waste is considered to be a promising feedstock.[32]

The production process for ethanol made from cellulosic material, waste, or residues is a complex process that requires breaking down raw materials into fermentable sugars. Once the sugars are extracted from the feedstock, they follow the same process as ethanol from food and feed crops.

The production of second- and third-generation ethanol requires innovative technologies for biomass hydrolysis and pre-treatment. The demand for ethanol is likely to increase over the next two decades, which has intensified investigations performed worldwide towards the wider production of cellulosic ethanol on a commercial scale within the next decade.[33] The investigations performed are related to: (i) novel crops and biotechnology issues, (ii) novel microbial fermentation,[32] (iii) process efficiency improvements, and (iv) dual alcohol blends.[47] A number of pilot and demonstration plants are also developing novel routes to create bio-ethanol from commercial and municipal solid waste (MSW). To produce biofuels using ethanol, it is usually mixed with gasoline to result in a greener fuel. Importantly, ethanol is easily manufactured by biomass fermentation and can be stored and transported safely. Moreover, it is cheaply available in many countries. Hence, ethanol is a potential fuel that can be easily used in DR processes. Renewable ethanol is a relatively low-cost alternative fuel and is proven to be one of the most cost-effective carbon abatement tools in transport. It is widely available and offers the only realistic alternative to petrol. It is the only alternative fuel available that does not require entirely new methods and infrastructure, or major adaptions to the current vehicle fleet, to transport goods and people from one place to another.[18–23,27,28]

### 2.4. Bio-butanol

Bio-butanol is a four-carbon alcohol with formula C\textsubscript{4}H\textsubscript{9}OH, and it is less investigated and less popular on the biofuel market than ethanol. At room temperature it is clear liquid, immiscible with water, with a density lower than water but greater than methanol and ethanol. Bio-butanol can be produced using lignin as well as the carbohydrate components of biomass by using biochemical process in two stages, with a different enzyme for each stage.[19] During the first stage, biomass is converted into butyric acid (C\textsubscript{4}H\textsubscript{8}O\textsubscript{2}) and hydrogen. Then another enzyme in the second stage transforms butyric acid into butanol. The hydrolysis of starch, cellulose, or hemicellulose into simple sugars is not involved in the process.
2.5. Levulinic acid and derivatives

Levulinic acid (LA) is classified as a keto acid, with the formula CH$_2$C(O)CH$_2$CO$_2$H. It is derived from the degradation of cellulose and is a potential precursor to biofuels. This white crystalline solid is soluble in water and polar organic solvents. LA can be produced cost effectively and in high yield from renewable feedstocks in industrial processes.[4] The current levulinic acid price is 5–8 USD per kilogram, with a target price of less than 1 USD per kilogram.

Levulinic acid offers one of the largest families of value-added derivatives and by-products such as solvents [e.g., gamma-valerolate (GVL), methyltetrahydrofuran (MeTHF)], monomers [e.g., gamma-valerolactone (GVL)], fuel additives [e.g., levulinic acid esters (LA-esters)], herbicides [e.g., delta-amino levulinic acid (DALA)], and others. Levulinic acid derivatives can also be used to produce fuel additives as well as gasoline components. Methyltetrahydrofuran (MeTHF), a levulinic acid derivative, can be blended up to 50% with gasoline to increase the vehicle performance and reduce pollutant emissions. At large-scale production, MeTHF is competitive with common fuel oxygenates such as ethanol. MeTHF has a lower vapor pressure, so blending with gasoline is effective in reducing volatile organic compound (VOC) emissions. Today, fuel additives based on levulinic acid can replace cetane improvers, cold-flow improvers for diesel, and lubricity improvers.[32,48]

Renewable biodiesel can be produced by hydrogenating levulinic acid oligomer derivatives. Hydrogenation is used today for the production of biodiesel, by using vegetable oils and animal waste fats that have limited availability and a high price. Levulinic acid oligomers can be produced at large scale from biomass feedstocks and at a lower price to be hydrogenated in existing installations. The hydrogenated material formed can be further processed with existing technology to produce “drop-in” renewable biodiesel and renewable jet fuel.[32,48]

3. Fuel Processing

One of the most effective means of reducing IC engine emissions is the use of alternative gaseous fuels in place of PBE.[39] Among the gaseous fuels, syngas (named also as producer gas, town gas, blue water gas, or synthesis gas, depending on the formation method), which consists mainly of carbon monoxide and hydrogen, has been recognized as an environmentally friendly alternative fuel for the IC engine.[15] Mixtures of H$_2$ and CO could serve as an alternative spark ignition (SI) fuel due to their high anti-knock behavior and compression ignition (CI) engines.[50,51] The problem is that syngas produced from HC DR fluctuates in the constituent’s content, and the most appropriate bio-derived syngas composition that will give the best performance is unknown.

In principle, syngas can be produced from many different resources such as natural gas, naphtha, residual oil, petroleum coke, coal, and biomass, including biomass wastes.[15,52] Next-generation biofuels, such as cellulosic bio-ethanol, organic acids from waste, synthetic biofuels obtained via gasification of biomass, bio hydrogen, and others, are currently at the center of attention of technologists and policy makers who are in search of the more sustainable biofuel of tomorrow.[53] Lignocellulose-based feedstocks can be converted into gaseous or liquid fuels, namely syngas, or alcohols.[25,26] Ethanol is a possible fuel product from cellulosic biomass.[25,54,55] and there has been a significant increase over the past few years in the number of potential new fuel molecules, including methanol,[56,57] butanol,[58,59] longer-chain alcohols,[26,60] furan-based molecules,[61-63] and bio-derived synthetic hydrocarbons.[26,54,64-66] Importantly, lignocellulose (or cellulose) is the cheapest and most abundant source of biomass, whose properties make it a very attractive alternative fuel or fuel blend for the purpose of reforming.

Lignocellulose biomass typically contains 40–45 wt% oxygen, and oxygen removal further increases the fuel heating value. The more oxygen removed, the higher the energy density of the fuel; however, to improve the fuel combustion characteristics it may be desirable to leave some of the oxygen in the fuel.[53] The previous methods for lignocellulose biomass conversion require high-temperature treatments, greater than 723 K.[25] Lignocellulosic material can be converted into valuable fuels by three primary routes, as shown in Figure 5, including syngas production by gasification, bio-oil production by pyrolysis or liquefaction, or hydrolysis of biomass to produce sugar monomer units. Biomass gasification is a complex process that involves several reactions.[41,67] Fluidized bed steam gasification can maximize the gaseous product yield as a result of the high heating rate involved, advantageous residence time characteristics, and efficient tar reduction. However, the composition of syngas fluctuates due to many factors and the conversion of biomass to syngas is typically of low yield. It has been shown that gasification can produce approximately 0.62 kg of carbon monoxide and hydrogen synthesis gas from 1 kg of biomass, resulting in a conversion efficiency of 62%. Modern Fisher–Tropsch synthesis reactors can achieve efficiencies near 90% of the maximum theoretical conversion values.

As the specific objective is to effectively produce a syngas with specific composition, further improvement may be achieved by the catalytic reforming of methane and tar.[41] A preferred method for reducing tars is the catalytic decomposition at temperatures close to those in the operating gasifier.[5] This would improve the recovery of the carbon and hydrogen in the synthesis gas and reduce the organic loading of wastewater produced when the raw gas is cooled to remove steam from the raw product gas. Similarly, it would be preferable to reform methane in the raw gas before the gas is cooled, so that any CO$_2$ resulting from the methane reforming process can be removed in a single step along with the other inorganic gas impurities.

Instead of gasification, valuable liquid biofuels can be obtained by lignocellulosic biomass fermentation and microbe digestion. The lignocellulosic biomass to bio-ethanol process is complex and includes raw material pretreatment, hydrolysis, fermentation, and distillation. Usually, as a result from
100 g of raw material dry basis (32 g of cellulose), approximately 11 g of ethanol are obtained.

3.1. Principles of biofuel dry reforming

Dry reforming is an established process to produce hydrogen on an industrial scale. Currently syngas is mainly produced by the steam reforming reaction [Eq. (1)], with the hydrogen-to-carbon-monoxide (H₂/CO) ratio equal to approximately 3.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H^0_{298} = 206 \text{ kJ mol}^{-1} \quad (1)
\]

The efficiency of the process rise and then decrease with increasing pressure is a result of the reverse water–gas-shift reaction in which the hydrogen is reacted with the reactant CO₂ to produce water.

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H^0_{298} = -42.2 \text{ kJ mol}^{-1} \quad (2)
\]

The result of Equation (2) is that valuable hydrogen is wasted to form water. The first reaction is strongly endothermic, the second reaction is mildly exothermic, and the overall process taking into account both reactions will be strongly endothermic. This high energy consumption and increased concerns regarding the contribution of greenhouse gases to global warming have focused interest on the replacement of steam as reactant with carbon dioxide.

For the production of synthesis gas and hydrogen, the DR of methane consumes 1.6 times more energy than steam reforming; however, it yields the possibility to convert major greenhouse gasses into valuable products. The catalytic conversion of HCs by reforming with CO₂ (dry reforming, DR) enables the use of HCs in the generation of synthesis gas with a low H₂/CO ratio. One interesting and sustainable option is bio-ethanol (in general bio-alcohols) DR which proceeds according to Equation (3).

\[
\text{C}_2\text{H}_6\text{O} + \text{CO}_2 \rightarrow 3\text{CO} + 3\text{H}_2 \quad (3)
\]

Ethanol DR primarily results in the formation of species such as H₂, CO, CH₄, H₂O, and C, which are described as value-added products having different applications, that is, as reactant in many reducing reactions (hydrogen, CO) or as a fuel in fuel cells (hydrogen, syngas). The formation of any other species by-products in significant quantities has not been reported in the literature. Previous studies have presented a thermodynamic equilibrium analysis and experimental data on thermal and catalytic ethanol cracking and DR at various CO₂/ethanol ratios using a carbon-steel catalyst. The authors showed that highest hydrogen and carbon yields were obtained at 823 K. It was evidenced that in both catalytic dry reforming and the cracking of ethanol, carbon deposits were in the form of carbon nanofilaments. The other thermodynamic study reported optimum conditions that produced over 94% yield of syngas and complete conversion of ethanol without carbon deposition. The optimum conditions for hydrogen production were identified as follows: reaction temperatures between 1200 and 1300 K and carbon dioxide-to-ethanol molar ratios of 1.2–1.3 at 0.1 MPa. Under the optimal conditions, the complete conversion of ethanol, 94.75–94.86% yield of hydrogen, and 96.77–97.04% yield of carbon monoxide were achieved in the absence of carbon formation. Moreover it was shown that inert gases have a positive effect on the hydrogen and carbon monoxide yields.

The final composition of the produced gas is determined by the reaction conditions (i.e., pressure and temperature). The syngas produced by Equation (3) has a high carbon monoxide content and this process yields syngas with a low...
H₂/CO ratio (~1), which apart from IC engines could be also used for the synthesis of valuable products, such as hydrocarbons and oxygenates. As has been previously demonstrated, CO and H₂ gas mixtures are commercially converted (exoethermic reaction) to produce hydrocarbons (diesel or gasoline), methanol, and other fuels, for example, by using Fischer–Tropsch (FT) technology. Syngas can be also used as a source of pure hydrogen and carbon monoxide. Thus, hydrogen and syngas are the basic raw materials used to produce synthetic fuels (SLFs) and chemicals using industrially available processes.

The investigations related to DR are mainly focused on fuels such as natural gas, methane, and ethane, whereas the lignocellulose-based fuels/biomass waste DR is less studied, using similar catalysts systems. The Ni-based catalysts used for conventional methane or methanol reforming show good performance; however, they suffer from sintering, active component loss, coke formation, and poisoning, and therefore they might not provide sufficient, stable H₂ and CO gas streams required to produce fuel. Therefore, new nanomaterials/nanocomposites presenting high activity and durability and reasonable costs are sought to overcome this disadvantages for lignocellulose-derived biofuel DR.

4. Catalytic Screening: From HC DR to Biofuels DR Processing

In general, the most utilized catalysts for reforming can be divided into two types: non-precious metal (typically nickel) and precious metals from Group VIII elements (typically platinum or rhodium based), for which the active portion of the catalyst is reported to be the reduced metal. The commercial catalysts used for DR depend on the process regime and are usually bases on Ni, Ni with alkali metals, and/or noble metals, such as Pt, Pd, and Rh. The Ni-based catalysts produce good activity at high temperatures (973–1273 K); however, they tend to deactivate because of metal sintering and the high rate of carbon formation. Noble metals can be used to promote the Ni catalysts and to increase their resistance to deactivation. Although noble metals such as Pt, Rh, Ru, and Ir have also been reported for DR, yielding stable operation with low carbon formation/desorption on the catalysts during the reaction, their high cost and restricted availability make them unattractive in comparison with Ni-based catalysts. However, noble metals are considered to play a significant role in dehydrogenation and C–H bond breaking and also in the promotion of the water-gas-shift reaction (WGSR, Eq. (4)), which improves the overall catalyst efficiency towards H₂ formation. Thus, choosing the correct catalyst has a direct impact on the reaction rate and process efficiency, methane slip, and coke formation.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (4)
\]

Several types of commercial catalysts, based mostly on Ni components, are subjected to technical service every 3–8 years. To provide stable catalyst activity and selectivity over a desired period of time, usually 5–10 years, the content of the active metal component in the catalyst ranges up to 5%. However, in some cases, the active component content is more than 15% for low-specific-surface Ni/Al₂O₃ catalysts. To design catalysts that minimize deactivation, it is necessary to understand the elementary steps involved in the activation and conversion of HC and CO₂.

For CH₄ DR it was proposed that CO₂ participates in the CH₄ DR reaction by the reverse WGS (RWGS) reaction, yielding –OH groups that can then react with adsorbed CH₄ intermediates to form formate-type species (CH₃O). For a Pt/Al₂O₃ catalyst, it was suggested that CH₄ activation proceeds on free Pt sites, and CO₂ activation is assumed to be the rate-determining step, assisted by hydrogen to form adsorbed –CO and –OH. The participation of hydroxycarbonates and formates stabilized on the support in the reaction mechanism was also suggested for Pt/ZrO₂. Conversely, by using microcalorimetric measurements, it was demonstrated that for Pt/Al₂O₃ CO₂ is activated by direct interaction with the surface carbon atoms, which is the slowest step of DR. For the Ni/SiO₂ catalyst, transient studies revealed that CO₂ is activated by direct dissociation on Ni atoms, and the rate-limiting step is the interaction between C and O species adsorbed on Ni. For the Ni/La₂O₃ catalyst, a “bi-functional” mechanism was proposed claiming that methane is activated on the Ni particles, and carbon dioxide interacts with La₂O₃ to form carbonates, which scavenge carbon from nickel at the Ni–La₂O₃ interface. Hence, as dependent upon the support, even for the same metal, different routes of reagents activation and rate-determining stages seem to control the catalyst performance. However, it should be mentioned that according to previous studies for all traditional supports without noticeable oxygen mobility, reactivity, or supported metals, only CH₄ activation by C–H bond rupture is of any kinetic significance; all other stages proceeding much faster. It should also be emphasized that features of the CH₄ DR mechanism depend not only on the support and supported-metal interactions, but also on the operation conditions, namely, the concentrations of reagents, temperature, and oxygen mobility in the support. This requires a transient kinetic study under realistic conditions. Similarly, the oxygen mobility in complex oxide supports should be characterized not only in the standard oxidized state, but also after achieving steady state in realistic feeds (including when relatively weakly bound, for which mobile oxygen species are expected to be negligible).

A recent development that employs a new combination of the LaNiₓ₋₀.₅CoₓO₃ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) perovskites structures and iron oxide revealed that it was possible to reduce the carbon formation and attain good activity levels using this catalytic systems. It was shown that La–Ni perovskites exhibited high activity and selectivity without coke formation, and for La–Ni–Co perovskites, a trend was observed to decrease the catalytic activity by increasing the Co-doping level. Also it has been demonstrated that if a strong nickel–support interaction exists initially in the catalyst,
nickel sintering as well as carbon deposition can be avoided.\cite{42} Thus, on the one hand, nickel has to be inserted into a definite chemical structure rather than just dispersed onto it, which provides stabilization of nickel in the structure. Conversely, the catalyst has to be reducible under process conditions and must also be resistant to the mechanical stresses and easy to recover under process conditions. An attractive solution would be to associate nickel and the natural mineral structure (i.e., perovskites) because of the definite structure of the latter and its mechanical strength. Although such catalysts were very active even at low temperatures, a serious problem is their deactivation through coke formation, which leads to the reduction of the syngas production rate. Thus a development of inexpensive, highly durable, and active novel catalysts is of extreme interest.

Dry reforming requires the use of stable, effective catalysts that are resistant to coking; investigations should be focused on the metal activity, the resistance to coke formation, and the type of support that improves the catalyst efficiency.\cite{27,88} Recent publications present a large number of studied materials,\cite{25,41,67,69,72,78} however, there are only a few reports focusing on active catalyst development for lignocellulosic biomass-derived biofuels, and for such components the reaction mechanism and kinetic models are not well understood.\cite{16,25,44} Thermodynamic analysis indicated that dry reforming of ethanol is thermodynamically favorable above 590 K, which is much less than the value of methane DR (915 K).\cite{27} It was proposed for ethanol DR over the Ir/CeO$_2$ catalyst, that active metal Ir possesses a remarkable C–C bond dissociation capacity for ethanol conversion and the strong Ir–ceria interaction favors facile activation of water and/or oxygen to promote carbon removal.\cite{27} Dry reforming of ethanol has been studied by using a recyclable and long-lasting stainless-steel SS 316 catalyst and authors have obtained a hydrogen yield that is 98% of the theoretical value.\cite{20} A carbon-steel catalyst used to produce syngas and nanocarbon for ethanol DR has been presented elsewhere.\cite{88} Using Ni/Y$_2$O$_3$–ZrO$_2$ catalysts, a maximum CO$_2$ conversion of 61% at 800 °C was achieved.\cite{27} Another study showed that the interaction with the support and Ni reducibility depend on the support used.\cite{27} Among the supports used, the NiO species supported on CeO$_2$ and Al$_2$O$_3$ were the easiest to reduce, which resulted in undesirable reaction inhibition and enhanced the catalyst selectivity towards H$_2$ production.\cite{27}

The use of sonication as a green methodology in the preparation of nanocatalysts for reforming processes is of increasing in importance. It has been shown that the ultrasound-assisted preparation method induces uniform morphology without agglomeration of particles and also that the activity of synthesized nanocatalyst can reach thermodynamic equilibrium conversions with very good H$_2$/CO ratios. Mono- and bimetallic supported photo-active materials prepared by using ultrasound-assisted impregnation have been shown to present very interesting physicochemical properties in terms of very good active phase distribution, smaller particle size, higher specific surface area, uniform morphology, and excellent photocatalytic performance (Figure 6).\cite{89–94} It has been shown previously, that changing the surface morphology of active material and using nanostructured, multicomponent catalysts could be beneficial for the overall process efficiency.\cite{14,17,69,95–97} Moreover, it was shown that the catalyst surface can be tuned to obtain the desired properties and ratio between the electro-donating and accepting sites.\cite{95} Mono- and bimetallic supported photoactive materials synthesized by ultrasound-assisted impregnation,\cite{91,92} photodeposition,\cite{90,93,94} and low-temperature sol–gel methodologies\cite{88} are therefore very good candidates for bio-alcohol DR.

5. Future Prospects and Outlook

Biofuels, especially second-generation of biofuels, will be an important part of the future energy supply, mainly for the transportation sector. Similar to other possible sustainable energy sources they have advantages and disadvantages; however an important issue is addressed to maximize the sustainable energy production using biomass and avoid unacceptable environmental consequences.

Second-generation biofuels are recognized as necessary to meet health and environmental regulations. One of the most effective means of reducing IC engine emissions is the use of alternative gaseous fuels in place of PBFs. Among the gaseous fuels, syngas (also referred to as producer gas, town gas, blue-water gas, synthesis gas depending on formation method), which consists mainly of carbon monoxide and hydrogen, was recognized as an environmentally friendly alternative fuel for IC engines. The problem is that syngas produced from HC DR fluctuates in the constituent fraction. The energy content, the most appropriate syngas composition to result in the best performance is unknown. The syngas composition produced by biomass-derived alcohols reformed with CO$_2$ is also unknown, along with its effect on engine performance. Additional issues are fuel pre-treatment and catalysts composition. For this process a development of inexpensive, highly durable, and active catalysts is of high interest. As was mentioned above, noble metals enhance the conversion and
yield of hydrogen. However, the use of these noble-metal-based catalysts can make the process more expensive. Therefore, a clear advantage of using transition metals in terms of catalyst cost should be validated.

Assuming all of the above aspects, the development of sustainable energy sources, improvement in energy production technologies, and increased energy efficiency are mandatory but insufficient to meet the forthcoming legislation in view of the steady increase in global energy consumption. Conservation and rational energy management seem to be key to the issue and can help in reaching the agreed environmental requirements in Europe and worldwide (EU 20–20–20, COP21/CMP11).

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