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Catalysts for the Simultaneous Production of Syngas and Carbon Nanofilaments via Catalytic Decomposition of Biogas

Buthainah Ali Al-Timimi and Zahira Yaakob

Abstract

The possibility of alleviation of methane and carbon dioxide levels in the atmosphere are of major global interest. One of the alternatives that attracts much scientific attention is their chemical utilization, especially because both of these gases are components of the biogas. Thus, the rapid and extensive shale gas development makes them abundant raw materials. The development of an effective catalytic process that could be scaled-up for industrial purposes remains a great challenge for catalysis. As well, understanding of the mechanisms of molecular activation and the reaction pathways over active centers on heterogeneous catalysts needs to be advanced. It has been shown that biogas is a very interesting source of renewable energy. Because of its elevated methane content, biogas has excellent potential, as reflected in its year-over-year rise in production. This is because its manufacturing promotes the use of organic waste, prevents uncontrolled dumping and minimizes atmospheric methane and carbon dioxide emissions. Moreover, its use as an energy source is in some cases an alternative to fossil fuels and can help to minimize energy dependence. Another aspect of interest is that it can be used in situ, allowing agro-livestock farms or small industrial plants to achieve energy self-sufficiency.

Keywords: biogas, catalyst, renewable energy, decomposition, syngas, carbon nanofilaments

1. Introduction

Due to the elevated level of population growth, energy consumption has risen over the recent decade [1]. This increase in energy demand over the years has changed the energy scenario through manufacturing [2]. Furthermore, even with the current low oil price, the world's energy demand is anticipated to continue to rise in the future according to the international energy agency's new policy situation [3], from 13.2% in 2011 up to 17.6% in 2035 as shown **Figure 1**.

Currently, dependence on fossil fuels such as petroleum, gas and coal to satisfy energy demand has caused environmental issues owing to anthropogenic greenhouse gas generation. Methane (CH₄) and carbon dioxide (CO₂) are the most

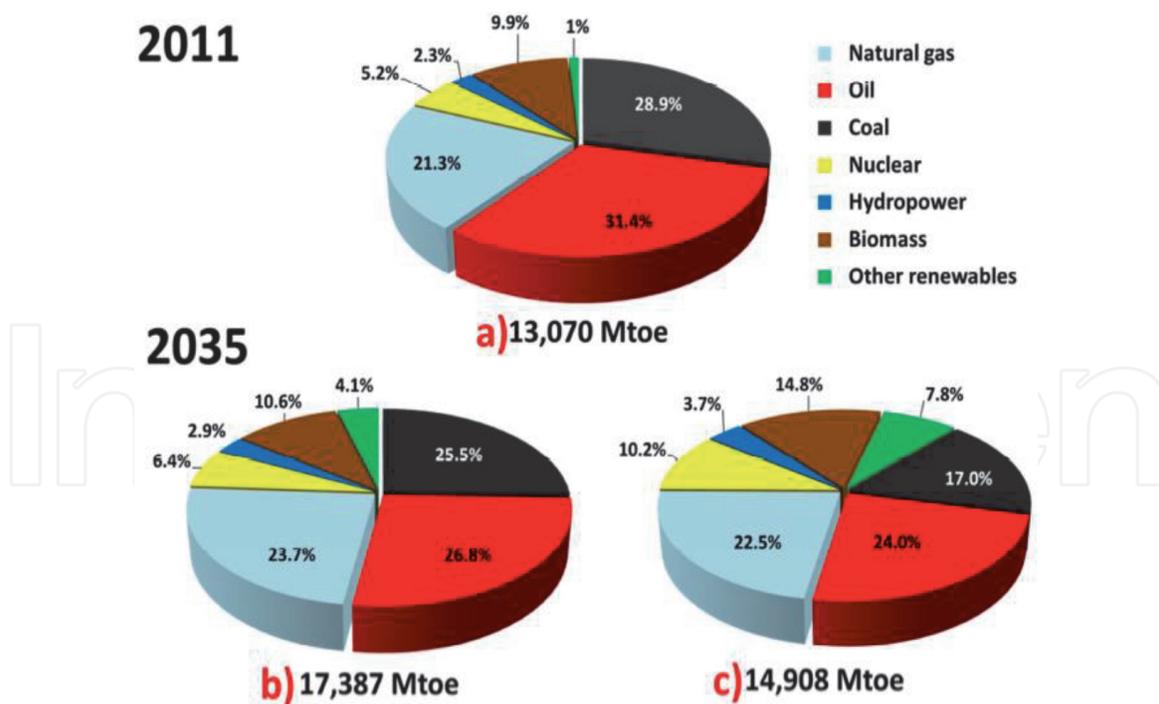


Figure 1. Primary energy demand in Mtoe (million tonnes of oil equivalent) (a) 2011, (b) 2035 “new policies scenario” and (c) 2035 “450 scenario” (adapted from Ref. [3]).

abundant greenhouse gasses and have lately contributed significantly to climate change issues [4]. While the level of methane in the environment is smaller than that of carbon dioxide [5], it is surprising that around 20% of worldwide warming occurs is caused by it [6]. Conventionally, there are two main sources of methane emissions including nature occurring activities and anthropogenic activities. Examples of the first source are termites, grasslands, coal beds, lakes, wetlands and forest fires, while examples from the second source are landfills, oil and gas treatment, wastewater treatment plants, coal mining, rice production, livestock and agricultural activities [7]. According to the US Environmental Protection Agency [8], methane manufacturing from landfill sites accounts for almost one-third of all methane produced in the United States alone, where landfill gas consists of 40–45% methane and 55–60% carbon dioxide by quantity by volume [9]. Notwithstanding, the reality that methane is a significant element of natural gas, a big quantity of natural gas is burned globally owing to technological constraints and the high price of carrying this valuable gas from its reservoirs, which are often far from industrial fields and the prospective market [10]. These actions have wasted an important source of hydrocarbons and contributed to global warming by releasing greenhouse gases into the atmosphere [11]. Carbon dioxide capture and storage (CCS) has been implemented globally to decrease carbon dioxide emissions due to pressure to combat global climate change and guarantee viable power sources [12]. In addition, renewable energy is required instantly to replace oil resources to decrease the heavy dependence on crude oil and its unwanted impacts on the atmosphere [13].

In the last few years, the resources of renewable energy, particularly, biogas, have gained massive attention around the world as a substitute for traditional fossil fuels [14]. In Southeast Asia, palm oil biomass is considered one of the most plentiful renewable resources and has enormous potential for the sustainable production of chemical substances and fuels. Liquid waste, known as palm oil mill effluent (POME) generated along with crude palm oil production, is one of Southeast Asia’s environmental problem due to its high pollution characteristics. Therefore, digestion, an aerobic treatment, is widely adopted in the oil palm industries as a reliable and

effective treatment for POME. The biogas generated during POME's anaerobic decomposition is not restored for use, but can be dissipated into the atmosphere [15]. The biogas produced contains two greenhouse gases: methane (60–70%) and carbon dioxide (30–40%) with traces of hydrogen sulfide which can be utilized after purification for heat generation, electricity production, bio-methane production and of synthesis gas (referred to as syngas, mixture of H₂ and CO) [16]. In fact, POME could become a significant source for biogas production due to its high organic content [17]. According to the World Meteorological Organization [18], methane and carbon dioxide levels were reported at 1845 ppm (parts per million) and 400.1 ppm (parts per million) respectively in 2015. Methane levels in the environment have been revealed to be below carbon dioxide levels, but have caused about 20% of worldwide warming [19]. Methane production was estimated at 6875 million metric tons which equals the total amount of carbon dioxide from all anthropogenic sources in 2010 [20]. Methane is frequently considered an important natural gas component with small amounts of other hydrocarbons such as ethane, propane and butane containing inert substances such as molecular oxygen (O₂) and carbon dioxide [21]. When monitoring the negative impact of methane and carbon dioxide, it is paramount to reduce their concentrations so that to avoid the high concentration of the greenhouse gases that lead to negative environmental conditions and increased temperature.

A great deal of extensive studies has been conducted to discover efficient methods of converting methane and carbon dioxide into precious products and thus reducing their elevated atmospheric quantity. Because of its comparatively low price and stability relative to other methods, converting carbon dioxide and methane into syngas is one of the most prevalent technologies [22]. It is one of the most important processes to convert hydrocarbons in the chemical industries to produce syngas [23]. In many distinct applications, such as Fischer-Tropsch (F-T) petroleum synthesis and the manufacturing of methanol and other precious fluid fuels and chemicals, syngas can be regarded as a construction block [24].

Recently, there have been many attempts that have prompted interest in producing alternative fuels by using renewable and environmentally friendly sources of energy, one of the few alternative sources is biogas. Even so, it is not entirely greenhouse gas-free; it does not, however, lead to global warming. Biogas is an appealing alternative for converting fuel to transport and generate electricity [25]. The vital route that will be of benefit to the power generation industry is the direct conversion of biogas, composed of methane and carbon dioxide to hydrocarbons under catalytic decomposition processes.

The use of catalysts in the catalytic reaction is essential in growing syngas manufacturing, as they assist to alter and enhance the reaction rate without consumption in the process [26]. Catalysts operate by offering an alternative mechanism that decreases energy activation, which implies the system needs less energy to achieve the state of transition. While catalytic reaction needs elevated temperatures to operate due to its heat-absorbing nature, the existence of catalysts can significantly decrease the reaction temperature [27].

Recently, there have been many attempts to use monometallic catalysts such as Ni, Co, Fe and Cu in the catalytic process because they are cheap and have a strong magnetization ability [28, 29]. Furthermore, bimetallic such as Ni-Co, Ni-Fe, and Ni-Cu have become very attractive to researchers due to their properties and the diversity of applications when compared with their individual mono-metal counterparts. The incorporation of nickel into Co, Fe, and Cu metals decreases the use of expensive noble metals [30]. Bimetallic catalysts success is thought to be due to the synergy of their parent metals they consist of two separate metals that display elevated dispersion and active sites. Moreover, the physical and chemical properties of the bimetallic catalysts are enhanced due to the formation of the solid solution

[31]. For example, Pudukudy et al. [32] and Pinilla et al. [33] revealed a greater carbon output from a bimetallic catalyst compared to a monometallic catalyst.

2. Energy and environment: current and difficult situations

At the moment, the adverse effect on the environment from the burning of fossil fuels, coal and compressed natural gas has become one of the main global issues [34]. Climate change occurs when the greenhouse effect rises, as demonstrated by flash floods, wind storms, heat waves and sudden droughts in a number of nations [35]. In addition, worldwide demand for energy is growing while fossil-fuel energy sources are quickly declining. Fossil fuels are one of the non-renewable energy resources that will be depleted in several decades if large-scale sources of energy are continually used [36]. As shown in **Figure 2**, the world production of fossil oil is at the peak of the production, and it is expected to diminish by the year 2050 [37]. Because of these situations, it is essential to replace petroleum consumption, minimize future expenses and eliminate the adverse effect on health and the environment. Thus, the replacement of non-renewable energy source with renewable resources is imperative to fulfill the needs of the energy demand without causing harm to the environment and mankind [38]. Due to this crisis, various kinds of energy are used to meet the large demand for petroleum-based fuel such as wind turbines, river dams, solar panels, geothermal power and biofuels [39].

The conversion of methane into liquid fuels or greater hydrocarbons has been performed extensively. Bradford and Vannice [40] studied the growth of methanol, formaldehyde, propanol, benzene and other aromatics through direct oxidative conversion of methane. Unfortunately, all the aforementioned processes produce low yields or they are not recommended for an industrial scale. Today, various technologies are available for the production of syngas from natural gas. This gas is a component of precious fluid fuels and chemicals like Fischer-Tropsch oil, methanol and dimethyl ether [41].

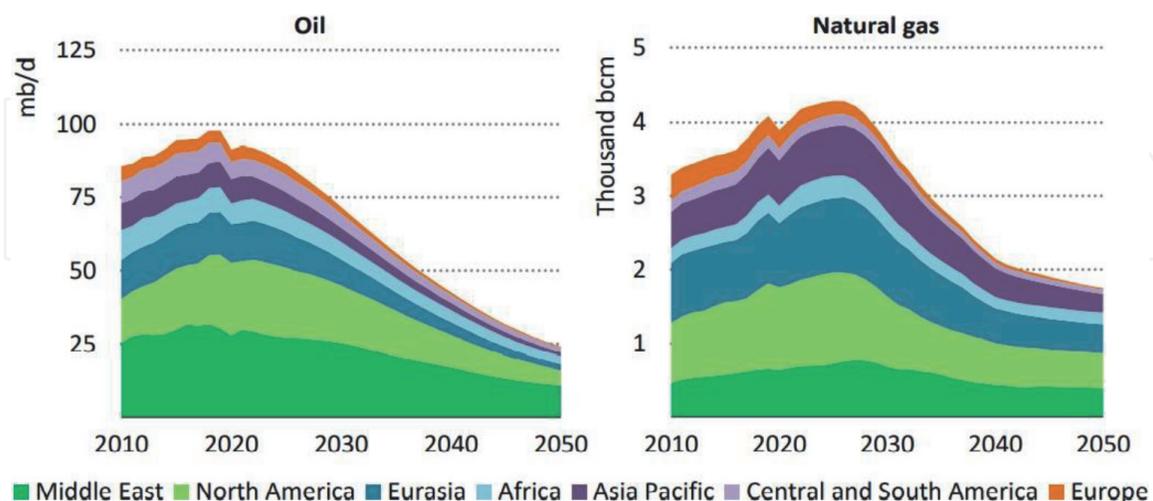


Figure 2. Oil and natural gas production in the NZE (adapted from Ref. [37]).

2.1 Biogas

The most significant renewable energy sources in the globe are biomass and hydropower. However, the use of other renewable resources is necessary to

minimize the negative climate impacts caused by the excessive use of fossil fuels. In that sense, biogas will play an important role in the future. The biogas primary energy has increased 70% between 2008 and 2013 [42] and its production is expected to double in 2022 up to $45 \times 10^9 \text{ m}^3$. Biogas is a gas consisting primarily of methane and carbon dioxide generated from anaerobic digestion of organic matter from agricultural waste, landfills, urban wastewater and industrial wastewater. It is considered, therefore, a renewable energy source [43].

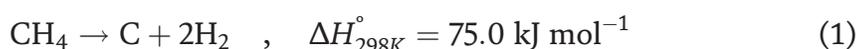
Based on the residue, biogas can contain traces of other compounds that hinder its use in the production of energy, making it necessary to install costly purification systems. Among them, the most significant are H_2S , NH_3 , halogenated hydrocarbons and siloxanes. Biogas has traditionally been regarded a non-value by-product usually burned in flares to avoid hazards to humans and the environment and then released into the atmosphere. Recently, various options for biogas use such as heat, electricity, mixed heat and energy or the manufacturing of bio-methane have been suggested. Nevertheless, from an economical point of view, all the previous biogas applications depend on government feed in tariff policies. Besides, different countries like Malaysia, Germany, Spain or Italy, have reduced or even removed the cost-based compensation creating an unstable scenario for the renewable energy producers [44]. Therefore, the manufacturing of fresh biogas products is not only interesting but essential in order to reduce the obstacles to profitability.

One of the alternatives considered is the manufacturing of syngas that consists of a blend of H_2 and CO and is the basis of C1 chemistry [45]. Depending on the syngas $\text{H}_2:\text{CO}$ ratio, it can be used to produce methanol, dimethyl ether (DME), liquid hydrocarbons (Fischer-Tropsch process) or H_2 . Syngas can be acquired from several procedures such as methane steam reforming, partial methane oxidation or dry methane reforming.

2.2 Catalytic decomposition of biogas

Due to overdependence on fossil-based fuels and increasing environmental concerns, the resources of renewable energy, in particular biogas, have gained massive attention around the world as a substitute for traditional fossil fuels. Biogas is obtained from the process of the anaerobic digestion of organic compounds. Methane (40–70%) and carbon dioxide (30–60%) are the primary compounds of biogas [46]. One of its most common applications is the direct combustion for energy recovery through co-generation plants that produce electricity and heat. Nevertheless, the use of renewable sources of methane like the one contained in biogas (bio-methane) for different applications like the production of hydrogen is a more interesting option than the use of fossil methane [47].

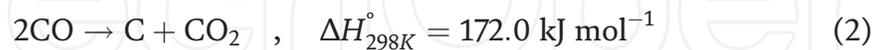
In this context, the catalytic decomposition of methane (CDM) (Eq. (1)) is being studied as an alternative to steam reforming of methane (SRM) to produce CO_2 -free hydrogen. The CDM in a single step produces a mixture of hydrogen and unconverted methane, which can be directly used as fuel in internal combustion engines or, even directly used to power a fuel cell [47].



The catalysts traditionally used in the CDM consist of transition metals belonging to group VIII (Ni, Fe, Co) supported over different metal oxides such as Al_2O_3 , MgO , La_2O_3 , and CeO_2 [48, 49]. These catalysts are characterized by promoting the formation of carbon nanostructures (carbon nanofibers or carbon nanotubes) varying their textural and structural properties as a function of the catalyst composition and the operational conditions [50]. These carbon nanostructures have very

interesting properties for their use in applications where thermal and electrical conductivity of materials is a key factor. However, one of the problems of the CDM is the deactivation over time of the catalysts due to carbon deposition that encapsulates the metal particles disabling their active sites [51].

Co-feeding with CH₄ different oxidizing agents such as H₂, H₂O or CO₂, can increase the life of the catalyst. Co-feeding with H₂, inhibits the deactivation of the catalyst at the expense of a desired product, which reduces the efficiency of the process while the use of CO₂ as Co-feeding induces Boudouard reaction (Eq. (2)) thereby resulting in gasification of graphitic carbon produced during the CDM reaction.



The use of CO₂ in the CDM process has been studied by two approaches: some authors have suggested a cyclical process consisting of a methane decomposition step followed by another stage of gasification of the deposited carbon with CO₂. Other authors have studied the decomposition of mixtures CH₄:CO₂ in conditions that favor the formation of nanostructured carbon. Nagayasu et al. [52] observed a slow deactivation of a Ni based catalyst to be used in the CDM in the presence of CO₂. They also noted an increase in carbon accumulation capacity in the form of nanotubes by increasing the partial pressure of CO₂ co-fed along with that of CH₄.

Asai et al. [53] confirmed the inhibition of the deactivation of the catalyst studied in the decomposition of methane in the presence of CO₂, suggesting a mechanism based on the gasification of graphitic carbon layers that encapsulate the catalyst particles, allowing the formation of carbon in the form of nanotubes. Indeed, co-feeding of CH₄ and CO₂, which are the main components of biogas as previously mentioned, modifies the reaction mechanism of methane decomposition into carbon and H₂, to a process called dry reforming, which produces a mixture of H₂ and CO. This is a highly endothermic reaction that takes place by way of a catalyst in the temperature range between 600 and 800°C, producing syngas with a molar ratio 1:1 [54].

This syngas can be used in multiple applications such as fuel for solid oxide fuel cells or Fischer-Tropsch synthesis to produce environmental friendly liquid fuels, when using a renewable source such as biogas [55]. If the aim is to produce H₂, then a water gas shift reaction followed by CO₂-H₂ separation should be accomplished. The practical implementation of the dry reforming of methane (DRM) faces many key challenges, which also apply to the biogas decomposition, and one of the most important is the deactivation of the catalysts due to the formation of carbon during the reactions of CH₄ decomposition and CO₂ disproportionation [56]. Also, Edwards and Maitra [57] reported that it is convenient to work at high temperatures and low ratios of CH₄:CO₂ (<1), to minimize carbon formation from a thermodynamic point of view. However, from the industrial point of view it would be much more desirable to work at moderate temperatures and CH₄:CO₂ ratios close to one, despite these are conditions under which carbon formation is thermodynamically favored.

Another issue that should be addressed is the high sulfur content of the biogas. This can provoke severe metal catalysts deactivation, therefore an exhaustive desulphurization of the biogas fed to the catalytic decomposition of biogas (CDB) reactor would be required when using a real biogas. The most commonly used methods for hydrogen sulphide removal can be found in [58]. The more active catalysts that promote the lower carbon deposition are precious metals, but its high price provokes that the most widely used catalysts for dry reforming are based on Ni, Co and Fe [59], which are the same catalysts traditionally used in the CDM.

Since the typical CH₄:CO₂ ratio in biogas composition is higher than 1 (CH₄ concentration in biogas can be as high as 70% depending on its origin), avoiding carbon deposition in the biogas decomposition reaction is not a task easy to accomplish. Thus, as previously mentioned, the presence of CO₂ along with the selection of optimum operating conditions for the deposition of carbon could prevent the rapid deactivation of the catalyst, resulting in a new biogas recovery process in which a gas with a suitable composition for its use in an internal combustion engine and carbon nanofibers (CNF) with multiple applications in sectors such as energy and transport are obtained. Direct decomposition of a gas simulating a typical biogas composition by means of metal catalysts under conditions that are favorable for carbon deposition has been studied by Muradov and Smith [60]. The problem associated to carbon deposition through decomposition of CH₄:CO₂ mixtures with ratio >1 was solved by adding small amounts of steam, prolonging the catalyst life. Some previous works by De Llobet et al. [61] focused on a study of CDB, conducted at moderate temperatures and using typical catalysts previously used in the CDM, promoting the formation of nanostructured carbon and syngas. As per their report, the Ni/Al₂O₃ catalyst exhibited high activity as well as stability, allowing them to obtain high CH₄ conversion together with the high-yield production of fishbone-like nanocarbon.

2.3 Chemistry of carbon dioxide

Figure 3 illustrates a key aspect of the thermodynamics of any possible CO₂ conversion. The figure also demonstrates the free emission of CO₂ from Gibbs and its associated substances. It is evident that CO₂ is an extremely stable molecule; it therefore requires significant energy input, optimized reaction conditions and (almost invariably) active catalysts for any chemical conversion of CO₂ into a carbonaceous fuel.

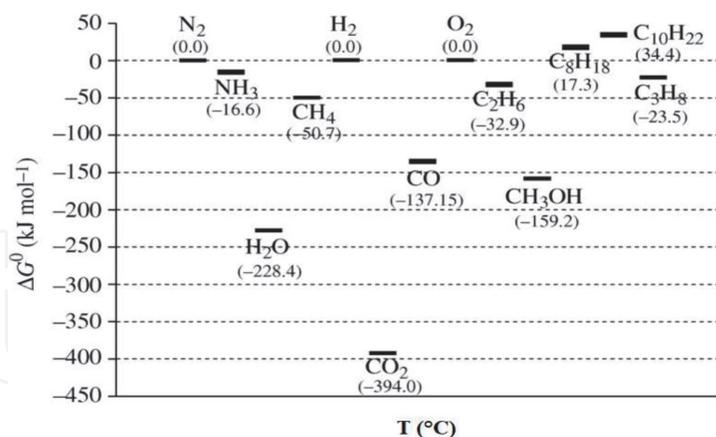


Figure 3. Gibbs free energies of formation of selected chemicals (adapted from Ref. [62]).

However, it is important to note that chemical reactions (conversions) arise due to the difference in the Gibbs free energy between the reactants and products of a chemical reaction (under certain conditions). This is illustrated by the Gibbs-Helmholtz relationship (Eq. (3)):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

Therefore, the comparative stability of the ultimate response products must be taken into consideration in the effort to use CO₂ as a chemical feedstock compared to the use of reactants. Both terms (ΔH° and $T\Delta S^\circ$) of the Gibbs free energy are not

favorable for the conversion of CO₂ to other molecules [63]. Since the carbon-oxygen bonds are relatively strong, substantial energy input is necessary for their cleavage, in terms of carbon reduction. Similarly, the entropy term ($T\Delta S^\circ$) makes little to no contribution to the thermodynamic driving force for any reaction involving CO₂. Most importantly, the enthalpy term, ΔH° , can be taken as a good initial guide for the assessment of thermodynamic stability and feasibility of any CO₂ conversions.

Freund and Roberts [63] highlighted the significant contribution of CO₂ surface chemistry. They claimed that any progress in the use of CO₂ as a useful reactant can be achieved in relation to fuel synthesis by using novel catalytic chemistry wisely. They attempted to illustrate that the greatest potential impact lies in this area of material chemistry, physics and engineering. These researchers also pointed out that a positive change in free energy should not be considered as a reason enough not to pursue potentially useful CO₂ reactions. This is because, ΔG° only provides information as to the yield of products at equilibrium through the relationship (Eq. (4)), and the kinetics of such a process is indeed favorable.

$$\Delta G^\circ = -RT \ln K \quad (4)$$

Since the kinetics are favorable, CO₂ decrease to CO (a key step in all conversion reactions), the primary step in all transformation responses, may also be feasible on metal surfaces or other catalytic materials, for instance on nano- and mesoporous metal particles [62]. Presently, a large number of industrial-scale chemical manufacturing processes worldwide operate on the basis of strong endothermic chemicals. The SRM to yield syngas and hydrogen is a classic example (Eq. (5)):

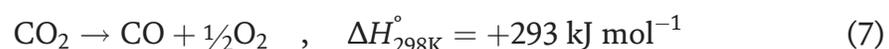


It is important to emphasize that the above-mentioned, highly endothermic reaction is used to produce large quantities of ‘merchant hydrogen’ in the gas, food and fertilizer industries worldwide. The corresponding DRM reflects the important reaction of CO₂ with hydrocarbons, which will be central to our idea of converting CO₂ into flue gases to produce chemical fuels (Eq. (6)):



The energy input for DRM requires about 20% more energy input than the SRM, but there is definitely no restricted additional energy cost for this chemical reaction. It is important that these two reactions lead to syngas with different H₂:CO molar ratios. For the final production of liquid fuels, both are useful for the formation of horns.

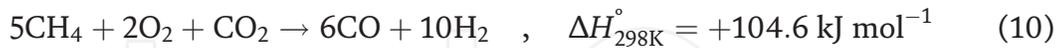
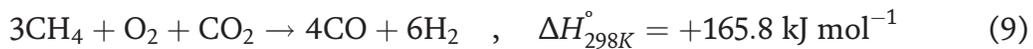
Figure 4 shows the enthalpy of the chemical reactions of the CO₂ conversion. This means that CO₂ is thermodynamically much easier to use as a co-reactant, usually with a higher (i.e. less negative) Gibbs free energy, such as H₂ or CH₄. These hydrogen-containing energy carriers give their internal chemical energy to promote the conversion of CO₂. Therefore, the heat of reaction (enthalpy of reaction) from CO₂ to CO production is important and obvious as the individual reactive and CO₂ energy as a key factor. Compare the thermal decomposition energies of CO₂ (Eqs. (7) and (8)).



With that of the reaction of CO₂ with H₂ (Eq. (8))



This aspect may be further illustrated by the process of ‘oxyforming’, whereby the amount of oxygen in the dry reforming reaction is increased deliberately. In doing so, the reaction enthalpy of reaction is significantly reduced (Eqs. (9) and (10)):



The fundamental material challenge in this area lies in the fact that, generally, the reaction between CO_2 and H_2 occurs at high temperatures on multi-component heterogeneous catalysts [64].

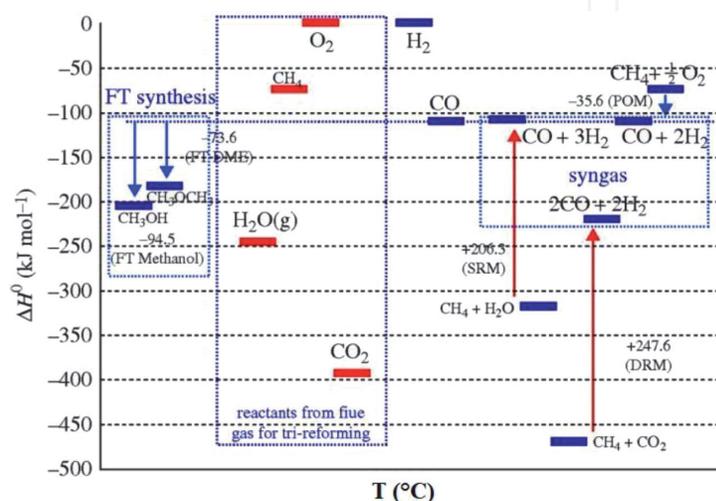


Figure 4. The enthalpy of reaction for syngas production and Fischer-Tropsch (FT) synthesis of methanol and dimethyl ether (adapted from Ref. [62]).

2.4 Syngas

Syngas is a blend of carbon monoxide and coal with a tiny quantity of methane and carbon dioxide. In the ever changing energy landscape, it is not only versatile, but also an increasingly important commodity. There are various carbon sources that happen through gasification or catalytic reformation for the manufacturing of syngas. Coal, natural gas (mainly methane), petroleum, and biomass could be the sources of carbon. The primary technical problem with fossil fuel syngas manufacturing is the complicated purification and conditioning procedures of syngas. The main reasons why the world has become more interested in the producing of biomass-derived syngas are therefore to decrease over-dependence on fossil fuels, to impose stricter CO_2 emission standards and to verify the accessibility of resources. Roddy [65] claimed that biomass could originate from industrial, domestic, agricultural and urban waste sources as a feedstock for syngas production. The use of biomass or waste as the raw material for syngas manufacturing is theoretically two-pronged: the generation of clean energy and an effective way to reduce waste as reported by Markets and Markets [66], a compound annual growth rate (CAGR) of 8.7% is anticipated to achieve 117,400 MW (Megawatts) heat in 2018. Boerrigter and Rauch [67] estimated the future market for syngas to increase to 50,000 petajoules (PJ) per annum, equivalent to 13.9×10^9 MWh per annum in 2040. This amounts to replacing an average 30% fossil fuel usage is 10% of the complete world power consumption. They also projected that syngas will be used

primarily in gas-to-liquid (GTL) procedures, with 49% for gas-to-product (GTP) procedures and 39% for renewable gas and hydrocarbon manufacturing. In, 1993, Shell Malaysia built the world's first commercial GTL plant in Bintulu, Sarawak. Since, 2003, as many as for 14,700 barrels of high-quality GTL products have been produced per day. This is clearly an upgrade in the production from its original capacity of 12,500 barrels per day. As reported by the Borneo Post, Shell's GTL plant plans to invest RM (Malaysian ringgit) 48.36 million to rejuvenate its plant in Bintulu in, 2015. The world's largest GTL plant is located in Qatar, with a production capacity of 140,000 barrels of product per day.

In short, the development of the market for syngas is accelerating, the important increase in syngas consumption is due to its use as an energy precursor. The presence of CO, H₂ and CH₄ gases, which possess certain heating value, makes it highly in demand. Syngas also includes approximately 50% of natural gas's power density. Subramani et al. [68] reported that 1 kg of H₂ contains the same amount of energy as 2.6 kg of CH₄, which is equivalent to 3.1 kg of gasoline. H₂ is used at low temperatures because of its elevated energy content; fuel cells are used to produce electricity, power cars or even in the synthesis of Fischer – Tropsch. In addition to serving as an energy carrier, it has traditionally been used as a feedstock for the mass production of significant chemicals, such as methanol, ammonia or fertilizers.

2.5 Carbon nanofilaments

Carbon nanofilaments are nanometric filaments with diameters between 1 and 200 nm and lengths of up to several microns. These materials are composed mainly of graphite type carbon whose basic structural component is graphene [69]. Graphene can be defined as the combination of carbon atoms with sp² hybridization, where each carbon atom joins three others forming a flat hexagonal tessellation (basal plane or graphene layer) [70]. The parallel stacking of several of these layers' outcomes in graphite characterized by an elevated structural order and a distance of 0.3354 nm between the distinct graphene layers (crystalline domain or interplanar distance, d₀₀₂) (Figure 5).

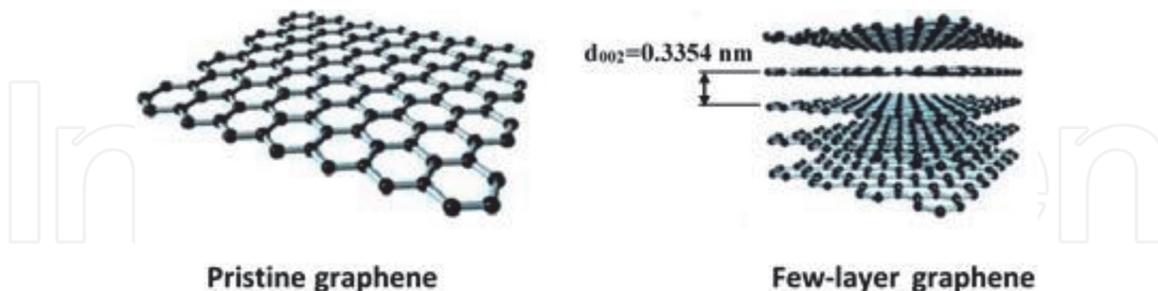


Figure 5.
Representative scheme of crystal structures of graphene (adapted from Ref. [71]).

On the other hand, carbon nanofilaments have a structural order inferior to that of graphite and according to the Franklin classification [72] correspond to turbostratic type materials, that is, they have crystalline domains greater than graphite and smaller than non-graphitic carbons ($0.3354 < d_{002} < 0.344$ nm).

Within carbon nanofilaments we can distinguish two types: carbon nanotubes (CNT) and carbon nanofibers (CNF). The CNT can be considered as layers of graphene rolled into hollow tubes [73]. Depending on the number of layers that make up the CNT, they are classified as single wall CNT (SWCNT), formed by a single layer, or multiple wall CNT (MWCNT), formed by 2 or more concentrically coiled layers (Figure 6a) [73]. On the other side, the CNF can be hollow or strong

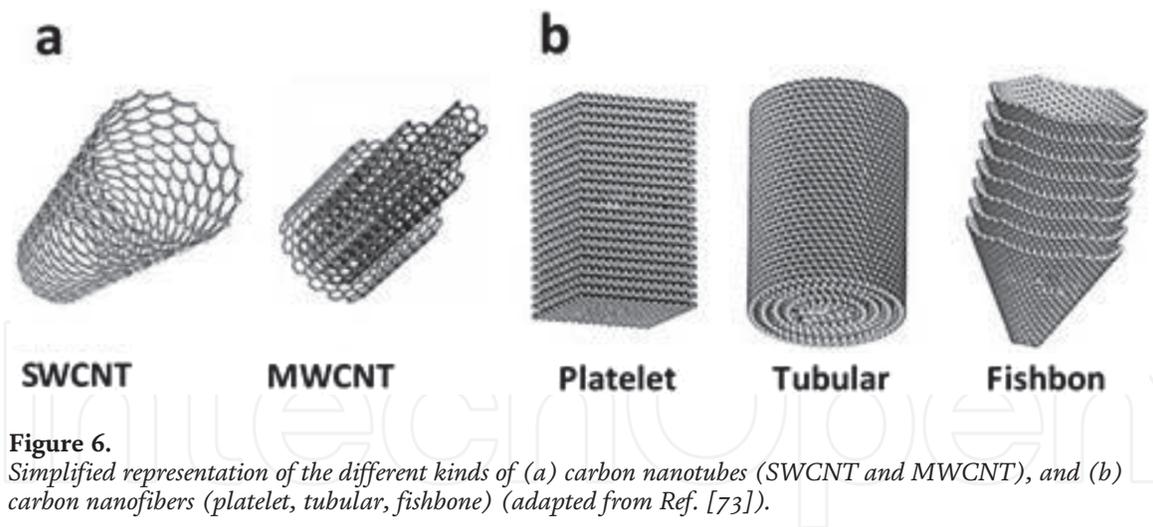


Figure 6. Simplified representation of the different kinds of (a) carbon nanotubes (SWCNT and MWCNT), and (b) carbon nanofibers (platelet, tubular, fishbone) (adapted from Ref. [73]).

and are categorized with regard to their longitudinal axis according to the angle they form graphene layers (α). The most common types of CNF are platelet, parallel (also named ribbon or tubular) and fishbone (**Figure 6b**) [73]. Platelet CNF are characterized by the fact that the graphene sheets are arranged perpendicular to the growth axis of the CNF ($\alpha \approx 180^\circ$), while in the fishbone type the angle α is between approximately $20\text{--}160^\circ$ [74].

They are also called Herringbone. Finally, the parallel types would be those in which the sheets are parallel to the longitudinal axis of the CNF ($\alpha \approx 0^\circ$). Unlike **Figure 6b**, this sort of structure can also be tubular and therefore it is not feasible to distinguish them from MWCNT by using electronic microscopy methods. However, there is some controversy, parallel type CNF tend to present areas along their structure in which the graphene layers are not oriented in parallel ($\alpha > 0^\circ$) as well as numerous imperfections such as the union of the layers' graphene inside the nanofiber (loops). Along with these three morphologies, in the CNF world there are other types of less common structures such as bamboo CNF, which are characterized by having internal holes that occur periodically due to the movement of the catalytic particle during the growth of the CNF, or the octopus-type NFCs that are generally produced when a Ni catalyst doped with Cu [75] is employed. Although there is a bibliography related to the formation of carbon filaments since the late nineteenth century, it was the discovery of the transmission electron microscope (TEM) in 1939 that really represented a breakthrough in this field since it allowed the observation in detail the morphology of this type of structures [76]. Initially, the interest in carbon formation derived from the problems that its accumulation caused in the processes of conversion of hydrocarbons (deactivation and destruction of catalysts or plugging of reactors) and therefore, the objective was to understand how and why it was generated in order to avoid their formation [77]. However, since the discovery of CNT by Iijima [78] in the 90s and due to the properties that carbon nanofilaments present (high specific surfaces and high electrical conductivities and thermal, the approach changed and numerous studies were initiated to optimize their production [79].

3. Current reforming technologies

Numerous reform techniques have been created to fulfill the long list of demands required in downstream chemicals procedures. Dry Reforming of methane is the most prevalent technique used in the syngas sector through one of three reforming procedures: (1) steam reforming of methane (SRM), (2) partial oxidation

of methane (POM) and (3) dry reforming of methane (DRM). The difference between the three techniques is based on the oxidant used, the kinetics and reaction energy, and the percentage of syngas produced ($H_2:CO$).

3.1 Steam reforming

The SRM approach produces a higher $H_2:CO$ ratio of 3:1 compared to the ratio required for Fischer-Tropsch (F-T) synthesis of 2:1 [80]. Due to its endothermic nature, SRM requires an extensive energy input so it is very expensive. In addition, a higher $H_2O:CH_4$ ratio is required to achieve a higher H_2 output, making the SRM process less favorable and speeding up the activation of catalysis. Moreover, SRM faces corrosion problems and requires a desulfurization unit [81].

3.2 Partial oxidation of methane

In the case of POM approach, this process is suitable for producing larger amounts of hydrocarbons and naphtha. Typically, POM has a very short residence time, high selectivity, and high conversion rates [82]. However, the exothermic nature of the reaction causes the induction of hot spots in the catalyst and makes it difficult to control the process. In addition, POM requires a cryogenic unit to separate oxygen from air. In the case of POM, this process is suitable for producing larger amounts of hydrocarbons and naphtha. POM typically has a very short period of residence, high selectivity and high conversion rates. The exothermic nature of the response, however, allows warm spots in the catalyst to be induced and makes the method hard to regulate and POM requires a cryogenic unit to separate oxygen from air [83].

4. Dry reforming of methane

DRM approach is the most promising of all techniques, as it utilizes two greenhouse gases (CO_2 and CH_4) to generate industry-significant syngas while at the same moment lowering excessive greenhouse gas emissions. The DRM method is also cheaper than other techniques, as it eliminates the complicated gas separation of finished products. It generates the ratio $H_2:CO$ that can be used to synthesize oxidized chemicals and F-T synthesis long-chain hydrocarbons. DRM can also be extended to biogas (CO_2 , CO , and CH_4) as a raw material for cleaner and eco-friendly fuels. DRM syngas is also a solar or nuclear energy storage facility [84]. Since reaction is endothermic, the process is generally carried out at temperatures between 450 and 900°C. In addition, the utilization of a catalyst is required in order to obtain acceptable CH_4 conversions. The practical application of the DRM faces many significant obstacles and one of the most significant is the deactivation of the catalysts due to carbon formation during CH_4 decomposition and CO_2 disproportionate responses. Working at elevated temperatures and low $CH_4:CO_2$ ratios (<1) is useful from a thermodynamic point of perspective to prevent carbon formation. From an industrial point of perspective, however, work at mild temperatures and CH_4 would be much more desirable: CO_2 ratios close to one. Nevertheless, circumstances under which thermodynamic carbon formation is favored [85].

In this context, the DRM's attempts focus on developing a catalyst that demonstrates elevated activity and stability and low carbon formation and price at the same moment. In one of the first works related to the DRM, Fischer and Tropsch studied different metals belonging to groups 8, 9 and 10 (Ni, Co, Fe, Mo, W, Y, Cu). Among them, only Ni and Co showed a good activity ($X_{CH_4} \approx 90\%$). Years later,

Gadalla et al. [86] tested different commercial Ni-based catalysts, obtaining CH₄ conversions near 100% during 70 h of operation. Nonetheless, in order to avoid carbon deposition and catalyst deactivation they used CH₄:CO₂ ratios below 0.5 and temperatures above 900°C. Due to their high activity and lower carbon formation as compared to Ni, noble metals have been extensively studied as catalysts for the DRM [87]. However, their high cost and low availability make other metals more attractive from an industrial point of view. Due to their reduced cost compared to noble metals, Ni, Co and Fe were also widely researched and in the last years, bimetallic catalysts have stood out.

In order to synthesize an enhanced catalyst, these catalysts aim to potentiate the features of both metals. Ni-Co bimetallic catalysts showed a very healthy conduct among them. In any event, carbon deposition issues are even more important when using biogas. Biogas usually has higher CH₄:CO₂ ratios than one that ultimately leads to bigger quantities of carbon depositions that quickly deactivate the catalysts. However, distinct types of carbon are created during the decomposition of hydrocarbons and luckily not all of them are directly liable for the deactivation of catalysts. The sort and location of carbon atoms is more important than the amount generated when considering catalytic activity, according to Pinilla et al. [88]. Generally, only carbon encapsulation is directly liable for deactivation of the catalyst owing to active center coverage, while other carbon structures, such as carbon nanofilaments, can only cause operational issues when manufactured in big amounts as reactor blockage.

4.1 Kinetics and mechanistics of dry reforming approach

Studies of DRM's kinetics and mechanisms were conducted to determine an appropriate reaction rate model, either empirically or on the basis of a theoretical response mechanism to best suit the relevant experimental information and possibly describe the response rate and the chemical process. This understanding can further optimize the design and layout of the chemical system catalysts (the reactor), which can further improve DRM's overall development with more cost-effective technology [89]. Although, from a mechanistic point of perspective, steam reforming has received much attention, there has been a resurgence of interest in dry reforming over the previous centuries. A series of catalysts for DRM were researched as a consequence. This has resulted in a number of mechanistic measures for DRM being published in the literature. The DRM reaction mechanism was explored by Aldana et al. [90] over a Ni-based catalyst.

Aldana et al. reported that H₂ dissociates on Ni⁰ locations while carbon dioxide is activated on ceria-zirconia assistance to generate carbonates that can be hydrogenated into formats and then into methoxy species. This mechanism includes weak fundamental support sites for carbon dioxide adsorption and includes a stable interface between metal and support. Compared to Ni-silica, which activates both carbon dioxide and hydrogen on Ni⁰ particles, these characteristics lead in much better operations of these catalysts [90]. This mechanism is also supported by Pan et al. [91]. Meanwhile, Ayodele et al. [92] conducted a DFT analysis of the DRM over Ru nanoparticles supported on TiO₂ (101).

4.2 Influence of process variables on reaction rates

Extensive research was carried out to study the impacts of altering process variables on catalyst performance for the DRM reaction. This inquiry is essential as various process factors may result in variable catalyst performance [93]. The notion of activation energy should be considered as it will determine the response rate.

Table 1 tabulates the activation energy (E_a) values of CH_4 and CO_2 obtained from different types of Ni-based catalysts in DRM. For most catalysts, the activation energy of CH_4 is higher than that of CO_2 since the molecules of CH_4 are more stable than those of CO_2 . Therefore, more energy is required to activate the more stable molecules. Moreover, the basicity of the assistance for the catalyst has resulted to variations in the activation barrier. Kathiraser et al. [93] think the activation energy in DRM is fully dependent on the catalyst's type of catalyst support, promoter and bimetallic interactions.

Catalyst	Preparation method	Total flowrate (mg)	Catalyst Amount (kJ/mol)	$E_{a(\text{CH}_4)}$ (kJ/mol)	$E_{a(\text{CO}_2)}$ (kJ/mol)	Ref.
Ni/ Al_2O_3 (400–650°C)	Wet impregnation	28	500	—	64.4	[94]
4.82Ni/ Al_2O_3 (750–850°C)	Incipient wetness	100–980	—	242.67	115.86	[95]
7Ni/MgO (550–750°C)	Incipient wetness-impregnation	—	10	105	99	[96]
5Ni/Mg Al_2O_4 (600–800°C)	Co-precipitation	30	20	26.39	40.43	[97]
13.5Ni-2K/5MnO- Al_2O_3 (550–800°C)	Impregnation	400	50	113.8	—	[98]
0.3Pt-10Ni/ Al_2O_3 (580–620°C)	Sequential impregnation	100	5	112.55	98.74	[99]
8%Ni/ α - Al_2O_3 (550–750°C)	Wet impregnation	360	40	89.1	88.6	[100]

Table 1.

E_a values over several Ni-based catalysts for DRM reaction.

In the meantime, Cui et al. [100] conducted a thorough study of the DRM mechanism over Ni/ α - Al_2O_3 using steady-state and transient kinetic methods at 550–750°C temperatures. Their results show that the CH_4 dissociation and CO_2 conversion E_a values could be classified as follows: low (550–575°C), middle (575–650°C) and high (650–750°C). In low and high temperature areas, the response was constant but fluctuated in the region of medium temperature. It is suggested that the dissociation of CH_4 into CH_x and hydrogen species in the Ni active sites at temperatures above 650°C has attained a level of balance. In addition to the activation energy, it is essential to correctly formulate the suitable catalyst's inherent kinetic models based on basic measures in order to reach a compromise between economic feasibility and process effectiveness. However, this kinetics of reaction is affected by the reactants' mass transport. When eliminating the impact of mass transport, the conversions observed can be directly ascribed to the catalyst's inherent kinetics.

According to Kathiraser et al. [93], distinct gas hourly space velocities (GHSVs) need to be tested to eliminate internal mass transport resistance. The aim of this experiment is to verify that the conversions have reached a stable value and that a further shift in GHSV does not influence the conversion of reactants. The contact time, which plays a significant part in CO_2 and CH_4 conversions, is another consideration. When the contact time value is high, CO_2 or CH_4 conversions stay unaffected. The particle size of the catalyst should be held as small as possible to eliminate inner mass transport resistance, so that a further reduction in size does not impact conversions.

Kim et al. [101], explored the use of a CO_2 -photoacoustic signal (PAS) to analyze kinetically the DRM reaction on a Ni catalyst supported on Al_2O_3 and TiO_2 . They

discovered that the reason why mass flow rates low are used is because this method generates heat periodically because when a material absorbs a modulated laser beam, the photoacoustic signal is produced. It is essential to remember the characteristics of kinetic curves that act as the reaction mechanism's blueprints. These include the point of inflection, a brief period of induction or breakpoints. No particular GHSV can be found from all the results to eliminate the impacts of constraints on mass transfer. This indicates that the development of inherent kinetic models is critical in preliminary research.

4.3 Catalysts for dry reforming approach

Numerous studies on the development of active and coking-resistant DRM reaction catalysts have been published [102, 103]. Common DRM catalysts are backed by noble metal catalysts like Ru, Rh and Pt and backed by transition metal catalysts like Ni and Co [104–106]. The calculations for the result showed that noble Ru and Rh metals exhibit greater activity than Ni as long as the particle sizes and dispersion are the same [106]. While noble metals such as Ru, Rh and Pt in the DRM response are very effective and more resistant to coking than other transition metals, they are not readily accessible and are also costly [104].

4.3.1 Nickel based catalyst material

Ni-based catalysts are the most frequently used for commercial purposes on an industrial scale. In order to commercialize the industrial sector DRM response, the primary focus is on developing inexpensive and cost-effective catalysts with high activity and high carbon deposition resistance. Researchers performed research on the sort of assistance used and the impacts of adding promoters to Ni-based catalysts in order to define the most efficient way to enhance their coking resistance. In addition, latest efforts to enhance catalytic activity and inhibit carbon formation are aimed at combining two or three metals as active locations [105, 107]. Pre-treatment process preparation method and catalyst also play a crucial role in altering structural characteristics, implementing behavior decrease and enhancing catalytic efficiency [108]. Besides establishing the Ni-based catalyst with certain modifying agents in the catalyst preparation, the incorporation of Ni particles in the mesoporous aid could also enhance the conversion of reactants and the yield of products by preventing the sintering of metal particles and improving the metal-supporting connection. This metal produces desirable results due to the high specific region of mesoporous materials which can increase the dispersion of Ni particles on the supported catalyst [109].

In addition, the strong interaction between metal and support stabilizes the Ni particles incorporated in the mesoporous matrix. Multiple contact regions between the Ni particles and the support could improve thermal stability and support metal cooperation and support. The incorporation of Ni-based catalysts into mesoporous supports such as MCM-41, SBA-16, TUD-1, meso- Al_2O_3 and meso- ZrO_2 has, as reported in the literature, demonstrated high catalytic activity and high carbon resistance in DRM. Catalyst supports can also be synthesized from plants, which is crucial for the effectiveness of DRM catalysts. The use of polymers from trees has been an interesting region among scientists in latest years with the aim of increasing the velocity of chemical reactions. In addition to generating high-quality chemicals, catalysts installed on commonly accessible cellulose incur low manufacturing expenses [110].

Abimanyu et al. [111] reported that the main steps to synthesize catalyst supports are pretreatment and hydrolysis. Ni-based catalysts have been used

industrially as metal precursors in DRM, but the need to refine the metal to improve catalyst performance has recently attracted the interest of many scientists, as these particles demonstrated promising physical and chemical properties with elevated technological applications potential.

The preparation technique significantly affected a catalyst's physico-chemical characteristics and efficiency, according to Jang et al. [112]. It has therefore been noted that impregnation and co-precipitation are the most commonly used standard techniques of catalyst preparing. Another less prevalent technique for preparing catalysts is sol-gel, which generates a distribution of fine size. This method reduces the deactivation rate, offers high thermal resistance to agglomeration and creates a product of high quality compared to conventional methods.

A new non-thermal glow discharge plasma method has recently been developed to improve metal support interaction, boost the distribution of Ni particles and improve the activity and stability of the catalyst [113]. However, in comparison with simpler preparation techniques, plasma therapy is comparatively costly. This would improve the activity and stability of the catalyst in the DRM response by combining novel catalytic material and techniques.

Supported bimetallic catalysts demonstrate increased DRM activity and stability based on Zhang et al. [114] study. The preparation technique is one of the main variables responsible for the bimetallic catalyst's outstanding catalytic results. During catalyst preparing, the use of high calcining temperature outcomes in strong interactions between metal and support, which converts the catalyst into stable frame-like constructions. In particular, carbon formation is efficiently blocked during the catalyst decrease by using Ni-Co alloy compared to using single Ni sites. The synthesis method of different catalysts also affects the reaction effectiveness. For example, the method of co-precipitation may produce smaller sizes of metal particles compared to the use of wet impregnation.

4.3.2 Catalysts developed for CO₂ reforming

There are focuses on the development of DRM catalysts for catalysts with the following features: greater activity and greater stability towards coke formation, sintering, the formation of inactive chemical species and metal oxidation [115]. The catalytic efficiency could be improved by changing the catalyst's active sites by adding supports and promoters during catalyst preparing to increase conversion and selectivity [116]. **Table 2** shows several catalysts that have been developed recently, including Ni-based catalysts applied to the DRM reaction.

4.4 Catalyst deactivation

Deactivation of catalyst relates to loss of activity of catalyst during the response. It is the significant drawback of metal-based catalysts, as it not only creates product reductions that affect the response rate, but also costs industry millions of cash to replace the catalyst. Catalyst deactivation basically relates to three elements, according to Bartholomew and Farrauto [122] chemical, mechanical and thermal. Catalysts for metal reforming are frequently deactivated by coking, poisoning, fouling and sintering. **Table 3** describes the mechanisms of catalyst deactivation.

4.4.1 Poisoning

Poisoning relates to the powerful adsorption in the feed of chemical substances such as impurities. Poisoning of catalysts may be reversible (temporary) or irreversible (permanent) [122]. The catalyst may be retrieved by air oxidation or

Catalyst	Preparation method	GHSV (mL/gh)	Temperature (°C)	CH ₄ conversion (%)	CO ₂ conversion (%)	H ₂ /CO ratio	Ref.
Co-, Cu- and Fe-doped Ni/Al ₂ O ₃	Fusion	12,000	650	34–40	NA	NA	[30]
25–55%Ni/MeO _x (Me = Al, Mg, Ti, and Si)	Evaporation-induced self-assembly	48,000	600	76	NA	NA	[50]
Ni/Ce-Al ₂ O ₃ and Ni/Ce-Zr-Al ₂ O ₃	Wet impregnation	21,000	800	66.7–79.5	45.2–86.9	NA	[58]
5% Ni/MgAl ₂ O ₄	Microwave-assisted combustion	NA	850	83	—	≈1	[102]
5,10,15%Ni/MgAl ₂ O ₄	Homogenous precipitation	12,000	700	78	89	NA	[103]
K,Mg,Ce-2,8% Ni/Al ₂ O ₃	Wet impregnation	NA	160	31.6	22.8	2.2	[107]
5–100%NiH-Ce	Co-precipitation	20,000	550	35–55	35–45	0.55–1.60	[115]
5,10,15% NiMgAlCe	Co-precipitation	29,000	750	33–48	57–69	0.78–0.96	[116]
Pd, Pt-55%Ni-Cu/MgO·Al ₂ O ₃	Wet impregnation	48,000	675	84	NA	0.55–1.50	[103]
15%Ni/ZrTiAlO _x	Sol-gel & impregnation	45,000	600	85	95	0.95	[117]
10Ni + 3%Ce/8% PO ₄ + ZrO ₂	Wet impregnation	28,115.4	800	95	96	NA	[118]
Ni-Mo ₂ C/MgO	Sol-gel	30,000	850	90	85	NA	[119]
NiO–10Al ₂ O ₃ –ZrO ₂	One-step synthesis method	48,000	700	92	90	0.73	[120]
Ni-W/Al ₂ O ₃ -MgO	Co-precipitation	36,000	777.29	87.6	93.3	1	[121]

Table 2. Catalysts developed for the DRM reaction.

steaming to wash its surface for reversible toxicity. For irreversible poisoning, however, the toxins cannot be removed, so replacing current catalysts with a fresh batch is essential. Sulfur species such as hydrogen sulfide are common poisons in all catalytic processes with reduced metals as the active site. S-poisoning, as in procedures of F-T synthesis and steam reform, is always a disaster.

In 2011, Bartholomew and Farrauto illustrated the mechanism of sulfur poisoning [122]. Firstly, the S atom adsorbs or blocks the reaction or active sites of the catalyst physically (geometric effect). Then, the S atom alters the metal atoms electronically. The metal ions subsequently alter their adsorbability or their capacity to dissociate with reactant molecules like H₂ and CO. The S atom also alters the surface area and creates major catalytic characteristics alterations. This hinders the accessibility of adsorbed reactants to each other and thus slows down the adsorbed reactants' surface propagation. **Table 4** describes the typical poisons of industrial catalysts for different types of reaction. The avoidance of sulfur toxicity and sulfur strength can be improved by modifying the structure of the catalysts by

Mechanism	Type	Definition
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation (Sintering)	Thermal	Thermally induced loss of the catalytic surface area due to crystalline growth, support area and active phase support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor-solid and solid-solid reactions	Chemical	Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion Loss of internal surface area due to mechanical induced crushing of the catalyst particle

Table 3.
Mechanisms of catalyst deactivation.

Reactions	Catalyst	Poisons
Steam reforming	Ni/Al ₂ O ₃ , Ni	H ₂ S, As, HCl
CO hydrogenation	Ni, CO, Fe	H ₂ S, As, COS, NH ₃ , HCN, metal carbonyls
Automotive catalytic converters	Pt, Pd	Pb, P, Zn, S
Ammonia synthesis	Fe	CO, CO ₂ , H ₂ O, O ₂ , S, C ₂ H ₂ , Bi, Se, Te, P, VSO ₄
Catalytic cracking	SiO ₂ -Al ₂ O ₃ , Zeolites	Organic bases, NH ₃ , hydrocarbon, Na, heavy metals

Table 4.
Poisons of the industrial catalysts.

incorporating certain additives, such as molybdenum and boron, which adsorb sulfur selectively or change the response circumstances. According to Bartholomew and Farrauto [122], reduction in the temperature of steam reforming over Ni/Al₂O₃ catalysts from 800 to 500°C will decrease the strength of S adsorption, hence reducing sulfur poisoning from 5 ppm to only 0.01 ppm.

4.4.2 Sintering effect (thermal degradation)

Bartholomew and Farrauto [122], Christensen et al. [123], and Argyle and Bartholomew [124] describe the sintering of a heterogeneous catalyst as the loss of the catalytic layer, which is generally irreversible owing to the development of crystallite either on the supporting material or after thermal degradation in the active stage. Bartholomew and Farrauto [122] revealed two significant sintering parameters. The first is the sintering of temperature, including above the catalyst atmospheric temperature. The next is the sintering rate, which is impacted by the support structure and morphology, the metal particle size distribution, and the support's phase transition. These two catalyst sintering processes are crystallite migration (coalescence) and nuclear or vapor transport (ripening of Ostwald). Christensen et al. [123] outlined that crystallite migration involves entire crystallite migration followed by collision and coalescence. In the meantime, Argyle and Bartholomew [124] addressed that Ostwald ripening relates to the migration of

metal transport species emitted from one crystallite over the assistance or through the gas phase and caught by another crystallite. The author also stated that the sintering method is due to elevated temperatures and that owing to the presence of water vapor there is an increase in the sintering speed. Due to sintering impacts, **Figure 7** demonstrates the conceptual models of crystallite development.

Lif and Skoglundh [125] found that the co-impregnation of nickel catalysts with the oxides of alkali metals, alkaline earths or lanthanides suppresses the sintering effect. In addition, it was also shown that the catalyst preparation sequential impregnation technique improves the catalyst's stability towards sintering. To conclude, it is extremely desirable that it possesses the following characteristics for the growth of a fresh catalyst: heat resistance, coking resistance and stability in syngas manufacturing.

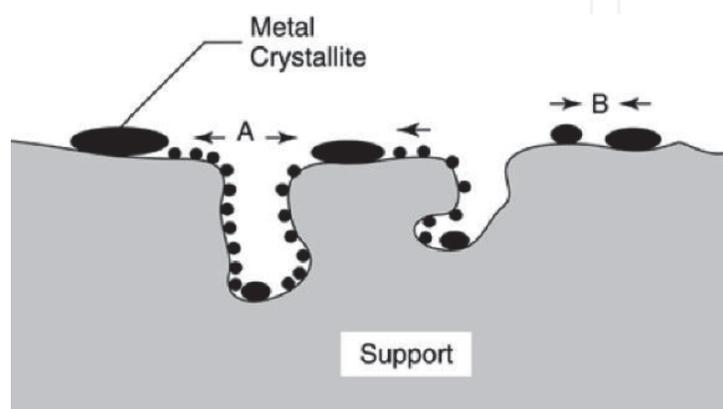


Figure 7. Conceptual models for crystallite growth due to sintering by (A) Ostwald ripening and (B) crystallite migration (adapted from Ref. [124]).

4.4.3 Carbon deposition

Fouling is a physical (mechanical) deactivation that causes the loss of catalyst activity owing to coke deposition that blocks the reactive sites. Steam reforming utilizes catalysts primarily based on Ni. Coke deposition is a prevalent cause of deactivation of Ni-based catalysts. Temperature-programmed hydrogenation (TPH) and Temperature-programmed oxidation (TPO) methods are used to analyze carbon deposition on the used catalyst. The methods of TPH and TPO are used to define the features of the kinds of carbon species created during reaction on the catalysts [126]. According to Bartholomew and Farrauto [122], the types of carbon that may be formed during reforming are C_α , C_β , C_V , C_γ and C_C (see **Table 5**).

CH_4 cracking (Eq. (1)) and CO disproportionation are the two primary reasons for coke deposition during DRM (Eq. (6)). There are three possible carbon fouling mechanisms for the metal catalyst. The first mechanism is carbon, which deposits reactive sites on the catalyst and impedes binding of the reactants to the active locations. The carbon would otherwise encapsulate the catalyst's reactive site and deactivate the catalysts. Another deactivation option resides in the coke being deposited in the catalyst pores, thereby stopping the reactants from crystallizing on it. The third mechanism involves carbon-forming needle-like filaments in the active site of the nickel catalyst, to some extent breaking the catalysts. **Figure 8** shows the conceptual model of the mechanisms of carbon fouling of a catalyst.

Quincoces et al. [135] used DRM catalyst $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$. They found that there were no rises in carbon deposition while the molar ratio of the reactants, CH_4/CO_2 , was maintained in unity. This finding shows that by changing the response circumstances, such as the molar ratio of reactant feed, carbon deposition can be

No.	Structural type	Designation	Temperature of formation (K)	Peak temperature (K) for reaction with H ₂	Ref.
1	Adsorbed, atomic (dispersed, surface carbide)	C _α	473–673	473	[127, 128]
2	Polymeric, amorphous films or filament	C _β	523–773	673	[127, 129, 130]
3	Vermicular (polymeric amorphous) a. filaments b. fibers c. whiskers	C _ν	573–1273	673–873	[127, 131–133]
4	Nickel carbide (bulk)	C _γ	423–523	548	[127]
5	Graphitic (crystalline) a. platelets b. films	C _C	773–823	823–1123	[127, 128, 131, 132, 134]

Table 5.
Forms and reactivity of carbon formed by decomposition of CO on Ni.

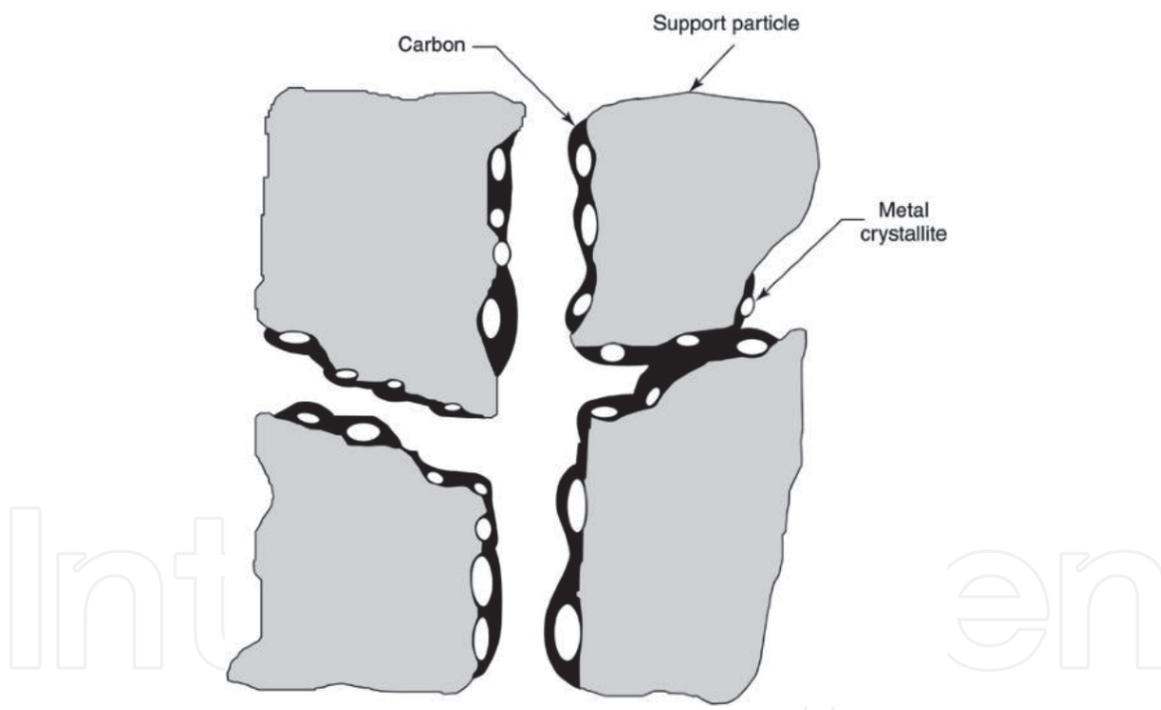


Figure 8.
Conceptual models of fouling, crystalline encapsulation and pore plugging of a supported metal catalyst (adapted from Ref [124]).

minimized. In their research, they discovered that a filamentous or whisker-like morphology was shown by the carbon deposit on Ni/ γ -Al₂O₃. This finding is comparable to Kępiński et al. [136] reporting. Meanwhile, on a backed metal catalyst, Toebes et al. [137] recorded carbon formation with metal crystallites in addition to carbon filaments. The growth of carbon filaments has pushed the metal crystallites from the surface of the catalyst support.

Ito et al. [138] also proposed that CO₂ could reduce the impacts of the fouling system. While the increasing carbon filaments remove the Ni metal, the introduced CO₂ responds to CO through a reverse-Boudouard response with the carbon

whiskers. One of the findings of their study was that after the removal of the carbon whisker, there is a decrease in bulk Ni. This renders the catalyst to be inactive for carbon deposition. However, there is an increase in the reforming activity of CH₄, which is due to the newly exposed Ni active sites from the bulk Ni.

Cheng et al. [139] report a reduction in the Brunauer-Emmett-Teller (BET) surface area and the amount of pore used carbon catalyst. As a result of this phenomenon, catalyst activity is lost. Wagner et al. [140] noted that a vapor reforming catalyst's acidity is proportional to its coke formation tendency. They also asserted that using basic support or basic mixed oxide support named K, the coking strength of the reforming catalysts could be improved. Li et al. [141] and Zanganeh et al. [142] also endorsed this argument, whereby nickel catalyst deactivation can be weakened if the nickel is backed by a strong Lewis base oxide like MgO, CaO, SrO or BaO.

Subsequently, the present research project introduces DRM to investigate the level of resistance of the catalyst towards carbon formation. Zanganeh et al. [142] suggested that an increase in the CO₂/CH₄ ratio during DRM and increasing the temperature to a high level may minimize carbon formation thermodynamically.

Ito et al. [138] also agreed that the increased CO₂-to-CH₄ feed ratio would eliminate the CH₄ decomposition reaction. Koo et al. [143] found that introducing less than 1wt percent of Mg into the Ni catalyst would enhance their coking strength. Adding promoter like Mo could therefore allay the coke formation phenomenon on the Ni catalyst. Another proposal to reduce the carbon deposition of a catalyst with a small surface area is to reduce the Ni load of the assistance. A CO₂/CH₄ molar ratio of more than 3.0 should be used to prevent the boudouard reaction.

5. Conclusion

Throughout this work, it has been shown that biogas is a very interesting source of renewable energy. Because of its elevated CH₄ content, biogas has excellent potential, as reflected in its year-over-year rise in production. This is because its manufacturing promotes the use of organic waste, prevents uncontrolled dumping and minimizes atmospheric CH₄ and CO₂ emissions. In addition, its use as an energy source is in some cases an alternative to fossil fuels and can help to minimize energy dependence. Another aspect of interest is that it can be used insitu, allowing agro-livestock farms or small industrial plants to achieve energy self-sufficiency. A lot of studies on DRM over Ni-based catalysts has been carried out in latest decades to better comprehend the mechanism and techniques of response to improve carbon deposition resistance. Several methods were suggested to minimize the trend of Ni-based catalyst coke formation. One is the use of the appropriate catalyst preparation technique. Another is the use of metal oxides with strong Lewis basicity as supports or promoters (since Lewis acidity is identified to encourage coke buildup). Future study in this area is likely to focus on the use of catalysts based on bimetallic nickel, such as the incorporation of Co with Ni catalyst.

The bimetallic catalysts showed stable activity and elevated inactivation resistance, although carbon deposition occurs. Catalyst activity should be considered, as the primary reason for catalytic inactivation is the encapsulating carbon, which is deposited directly in the catalyst's active places instead of the carrier's surface. Also, when it is generated in large quantities, it can cause clogging of the reactor. The problem of carbon formation is exacerbated when biogas is used for this process, because the CH₄:CO₂ ratio of biogas is greater than that which can lead to the formation of large carbon deposits in a short time. However, carbon atoms are more essential in type and place than the quantity of carbon generated. Averting the

deposition of carbon is therefore a challenging task. Also, this problem can be addressed from a completely different perspective. Rather than trying to avert carbon formation, it can be promoted as carbon filamentous. Previously, many researchers have effectively accomplished the synthesis of carbon filamentous through electric arc-discharge and laser ablation and chemical vapor deposition techniques. Nevertheless, the cost-efficient and the controlled synthesis of carbon filamentous with various morphologies by those techniques has not been reported.

Given the broad range of applications and the growing demand for biogas in different areas, the superb characteristics of biogas indicate its growing potential as a source of syngas for a broad range of renewable energies, where high purity and low manufacturing costs are significant factors. Thus, producing high-purity syngas and the controlled production of value-added carbon filamentous over cheap, efficient, tunable and simply synthesized catalysts is very important and is the main interest in this subject.

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Conflict of interest

The authors declare no conflict of interest.

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